

Inorganic Chemistry Part 2

CHAPTER 2

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p-Block Group 15 Elements The Nitrogen Family

OVERVIEW

- Group 15 elements of the periodic table are collectively known as pnicogens.
- The general electronic configuration of elements of group 15 is $ns^2 np^3$.
- Gradation in atomic and physical properties
 - Covalent radii:** $N < P < As < Sb < Bi$
 - Ionisation energy (IE):** $N > P > As > Sb > Bi$
 - Electronegativity (EN):** $N > P > As > Sb > Bi$
 - Melting point/K:** $N < P < Bi < Sb < As$
 - Boiling point/K:** $P < N < As < Bi < Sb$
 - Density:** $N < P < As < Sb < Bi$
- Nitrogen exists as a diatomic inert gas whereas others exist in tetrahedral tetraatomic forms P_4 , As_4 , Sb_4 and are solids.
- Metallic nature increases down the group.

N	P	As	Sb	Bi
Non-metals		Metalloids		Metal
- Due to inert pair effect, group 15 elements show variable oxidation states of -3 , $+3$ and $+5$. Stability of $+5$ oxidation state decreases down the group. Nitrogen besides -3 , $+3$ and $+5$ oxidation states, also shows -2 , -1 , 0 , $+1$, $+2$ and $+4$ oxidation states in its oxides.
- Nitrogen shows maximum covalency of 4, whereas others can expand their covalency to 5 or 6 due to the presence of vacant d -orbitals in their valence shell.
- Only nitrogen is capable of forming $p\pi-p\pi$ multiple bonds with itself and with carbon, oxygen etc. due to compatibility in size and high extent of overlap of orbitals. Phosphorous and other members do not form $p\pi-p\pi$ multiple bond but are capable of forming $p\pi-d\pi$ bond.
- Group 15 elements form hydrides of type, EH_3

Bond angle: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Acidic character: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Reducing agent: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
- Oxides of type X_2O_3 , X_2O_4 and X_2O_5 are formed by the elements of group 15.
 - Greater is the electronegativity more is the acidic nature of its oxides.
 - Acidic nature of each type decreases from N to Bi.

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
Acidic		Amphoteric		Basic

However, it shows feeble acidic character with strong alkali.

$$\xrightarrow{N_2O_5, P_2O_5, As_2O_5, Sb_2O_5, Bi_2O_5}$$

Acidic nature decreases
- Acidic nature of M_2O_4 oxides also decreases from N_2O_4 to Bi_2O_4 .
- Thermal stability decreases in each series from N to Bi.
 - In the oxides of a particular element, the acidic nature increases as the percentage of oxygen increases or the oxidation state increases.
- All the members of group 15 form oxyacids or oxoacids. The strength and stability of oxoacids having the element in same oxidation state decreases down the group.
- Except nitrogen, the rest of the elements of group 15 form two series of halides EX_3 and EX_5 . Nitrogen does not form pentahalides due to absence of d -orbitals in its valence shell.
- With the exception of N, all other group 15 elements form sulphides.
- For drying NH_3 , quicklime (CaO) is used. Other dehydrating agents like H_2SO_4 , $CaCl_2$, P_2O_5 cannot be used as they react with NH_3 .
- Nitrogen forms five oxides:**
 N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5
- HNO_3 also known as **aqua fortis** (meaning strong water) acts as monobasic acid. Noble metals like Au, Pt etc. dissolve in aqua regia i.e. $[3HCl (conc.) + 1 HNO_3 (conc.)]$
- Proteins react with HNO_3 to form a yellow compound called xanthoprotein.
- HNO_3 is used in manufacturing of explosives like TNT, picric acid, nitroglycerine etc.
- Phosphoric exists in number of allotropic forms. Important ones are white or yellow phosphorous, red phosphorous and black phosphorous. White phosphorous is the most reactive allotrope.
- Persons working with phosphorous develop a disease known as **phossy jaw**.
- Some of the important compounds of group 15 are as follows:

i. Scheele's green	$CuHAsO_3$
ii. Graham salt	$(NaPO_3)_6$
iii. Paris green	$(CH_3COO)_2Cu \cdot 3Cu(AsO_2)_2$
iv. Pearl white	$BiOCl$
v. Nitrophosphate	$Ca(H_2PO_2)_2 + 2Ca(NO_3)_2$
vi. Superphosphate of lime	$Ca(H_2PO_4)_2 \cdot H_2O + 2CaSO_4 \cdot 2H_2O$
vii. Thomas slag	$2Ca_3(PO_4)_2CaSiO_3$

- viii. Sindri fertilizer $(\text{NH}_4)_2\text{SO}_4$
 ix. Nangal fertilizer (CAN) $\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3$
 x. Amatol $80\% \text{NH}_4\text{NO}_3 + 20\% \text{T.N.T.}$
 xi. Ammonal $\text{NH}_4\text{NO}_3 + \text{Al powder}$
 (small quantity)
 xii. Swarts reagent SbF_3
 xiii. Tartaremetic (Potassium antimonyl tartarate)
 xiv. Angelis salt $\text{Na}_2\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$

22. a. Radioactive phosphorous (^{32}P) is used in the treatment of leukemia.
 b. In toothpaste, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is added as a mild abrasive and polishing agent.
 c. Amatol is $80\% \text{NH}_4\text{NO}_3 + 20\% \text{TNT}$ and is used as an explosive.

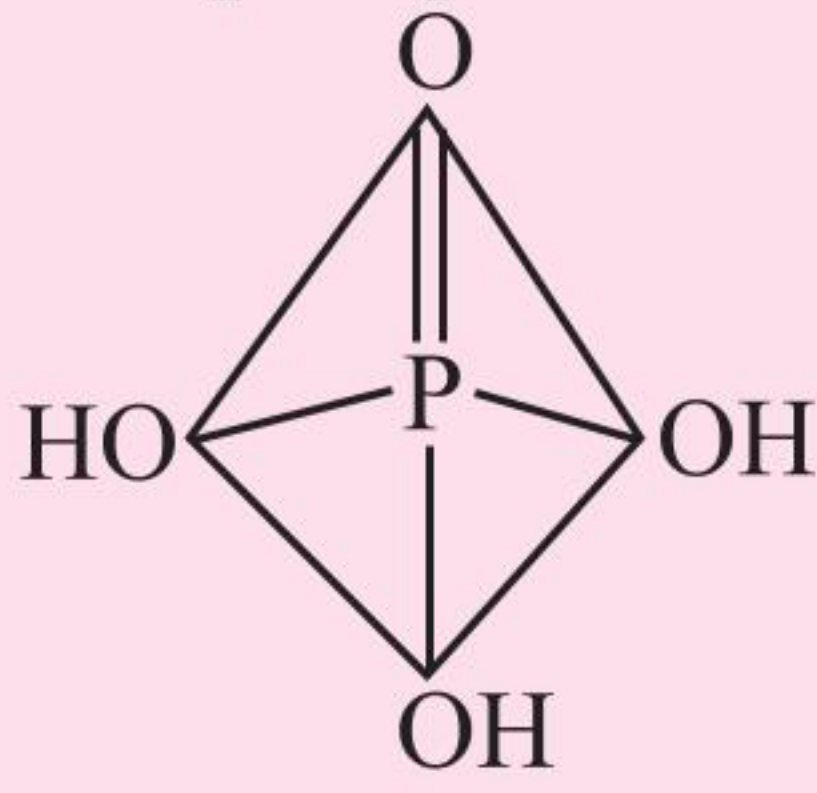
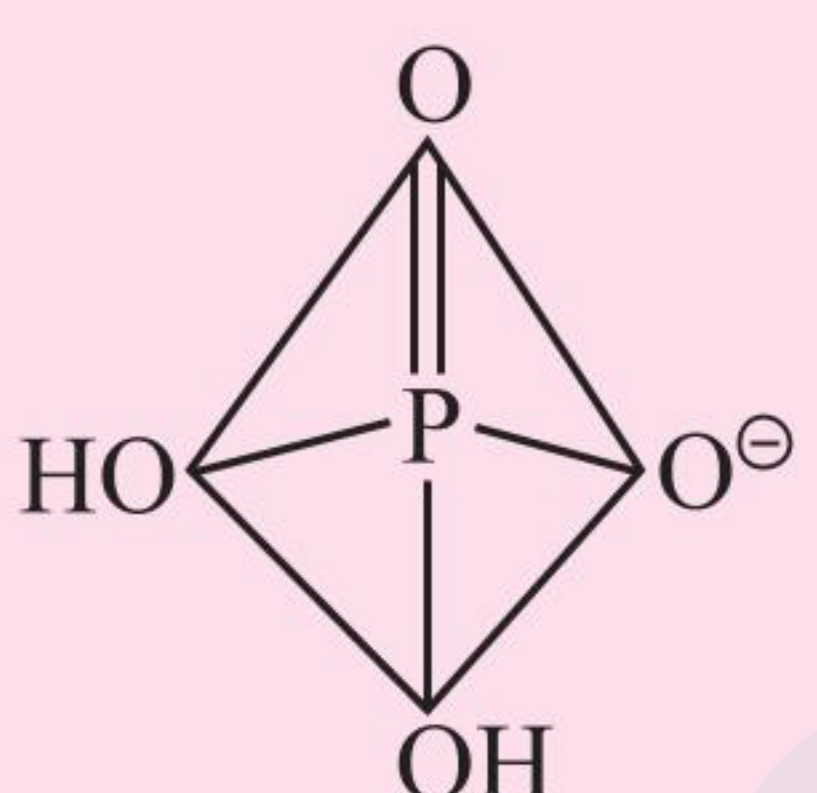
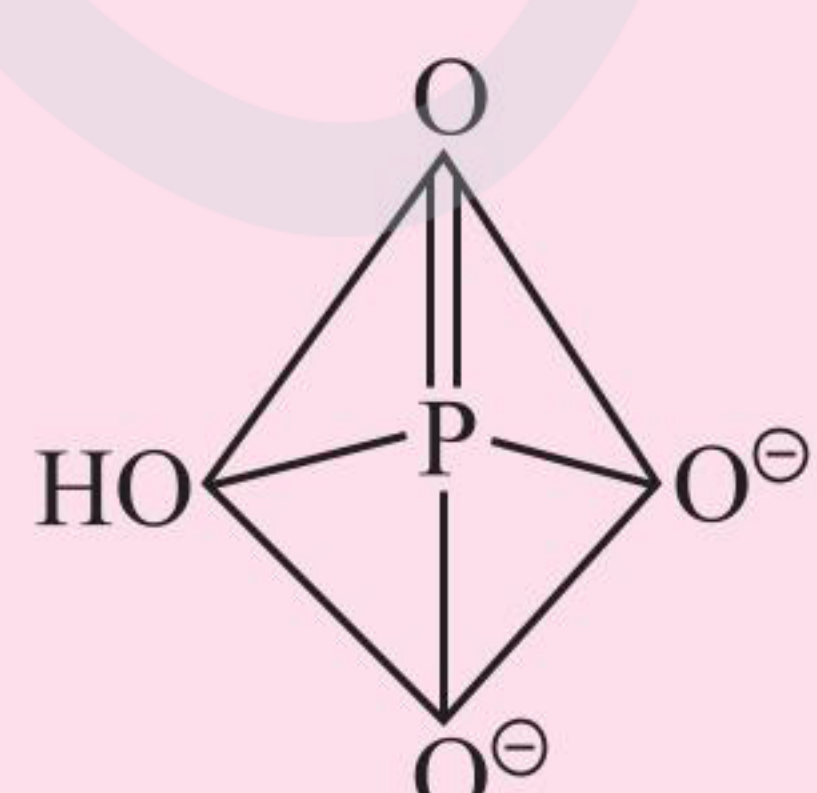
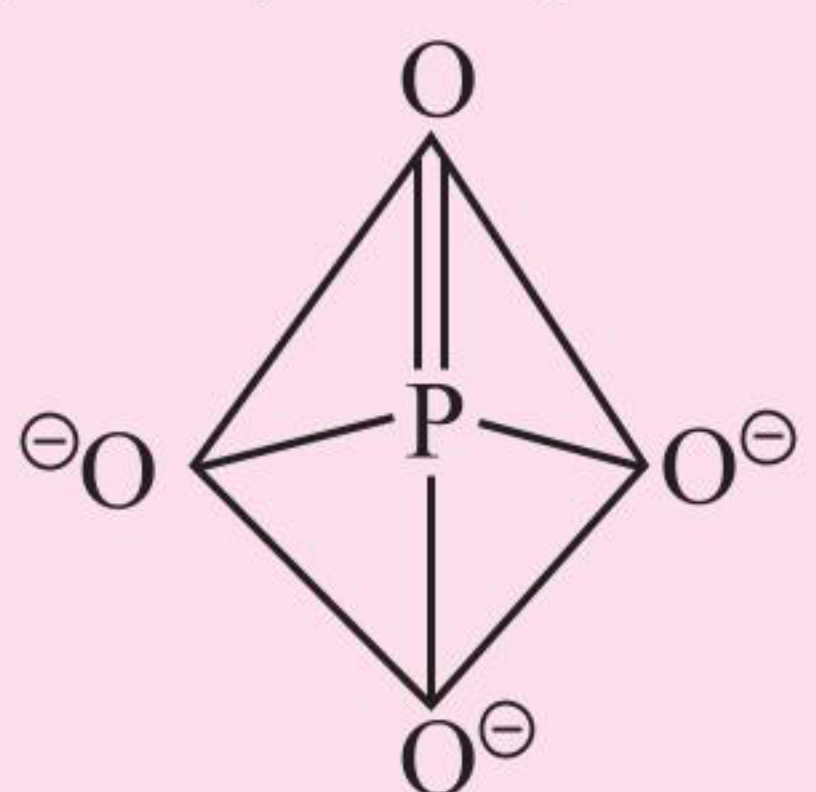
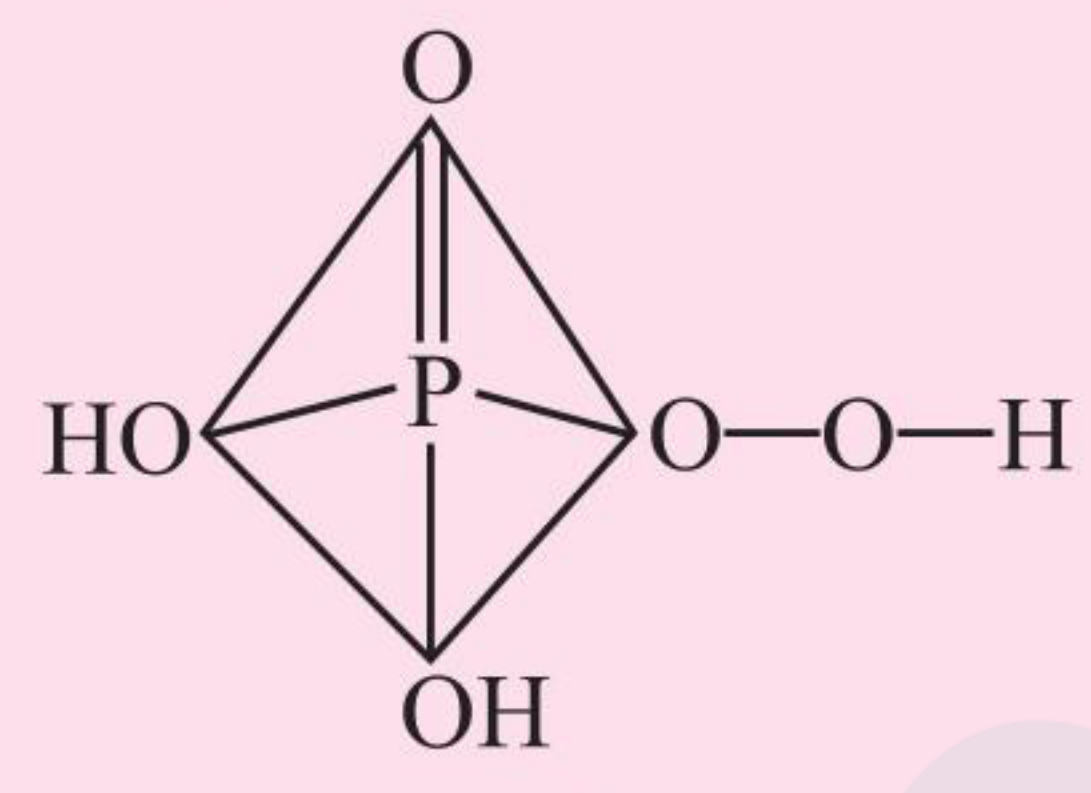
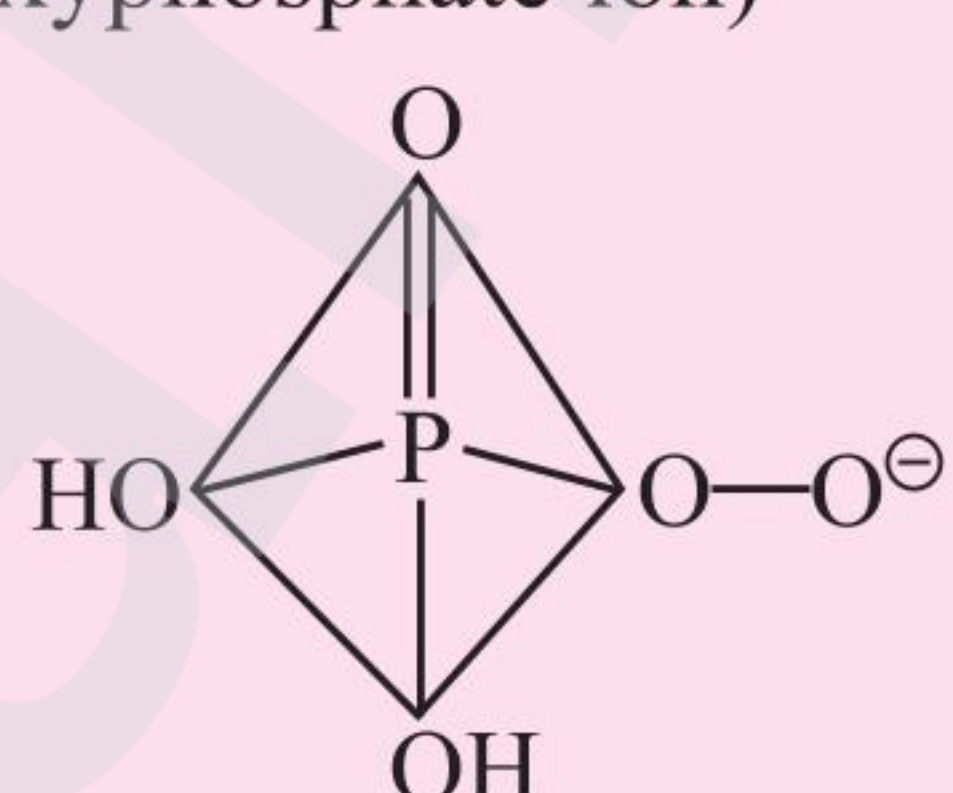
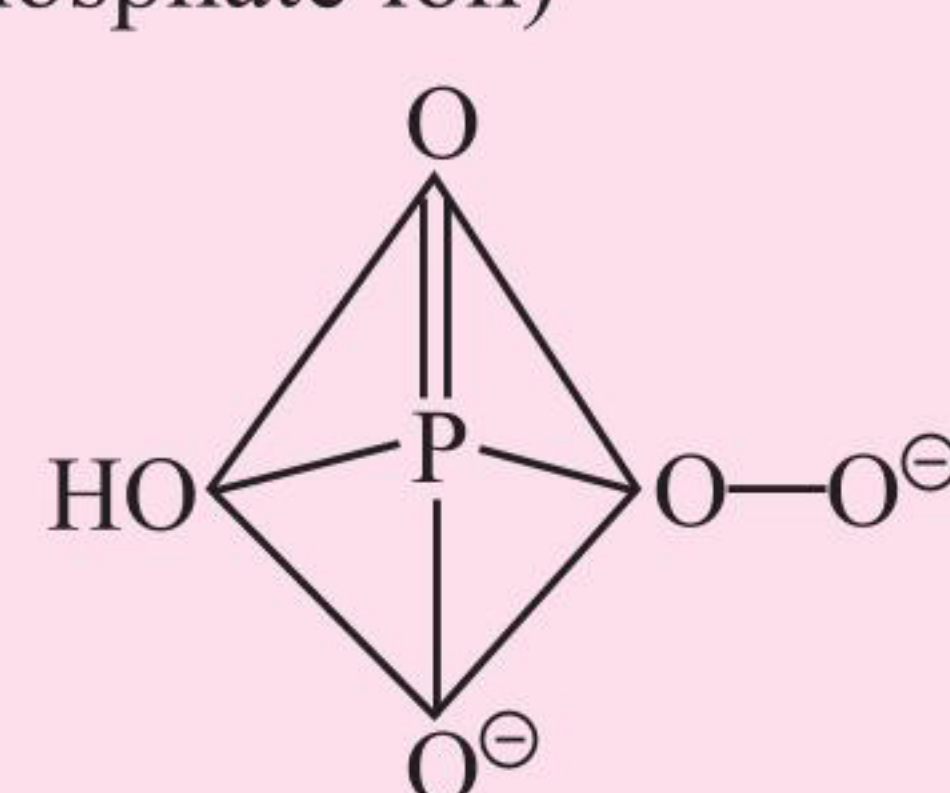
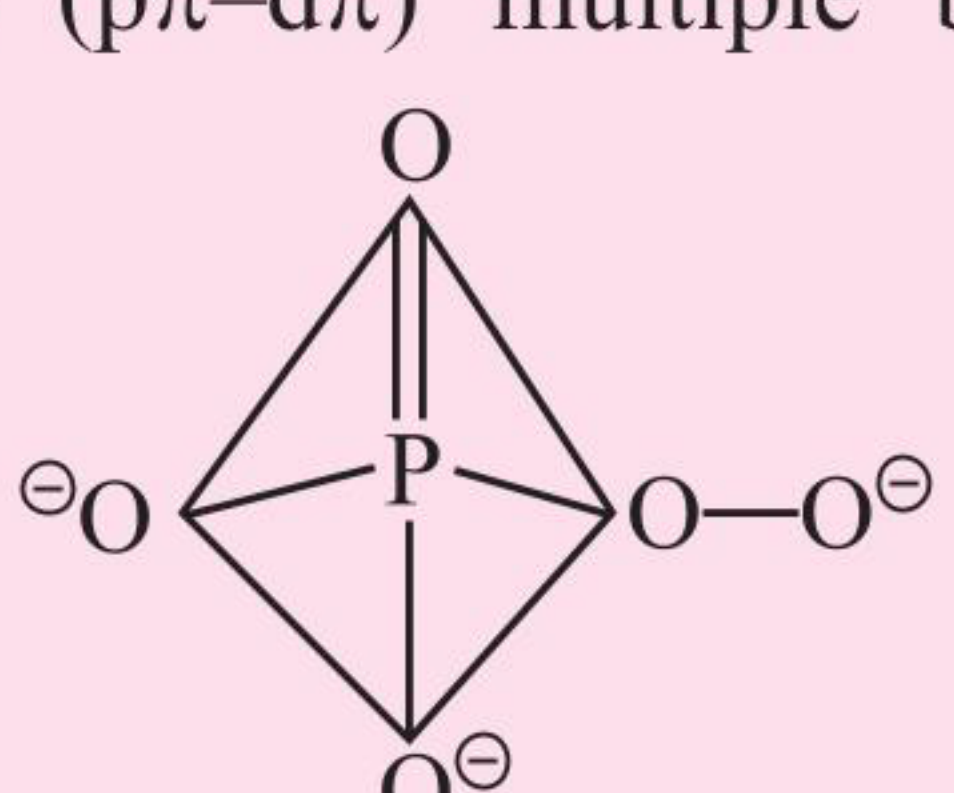
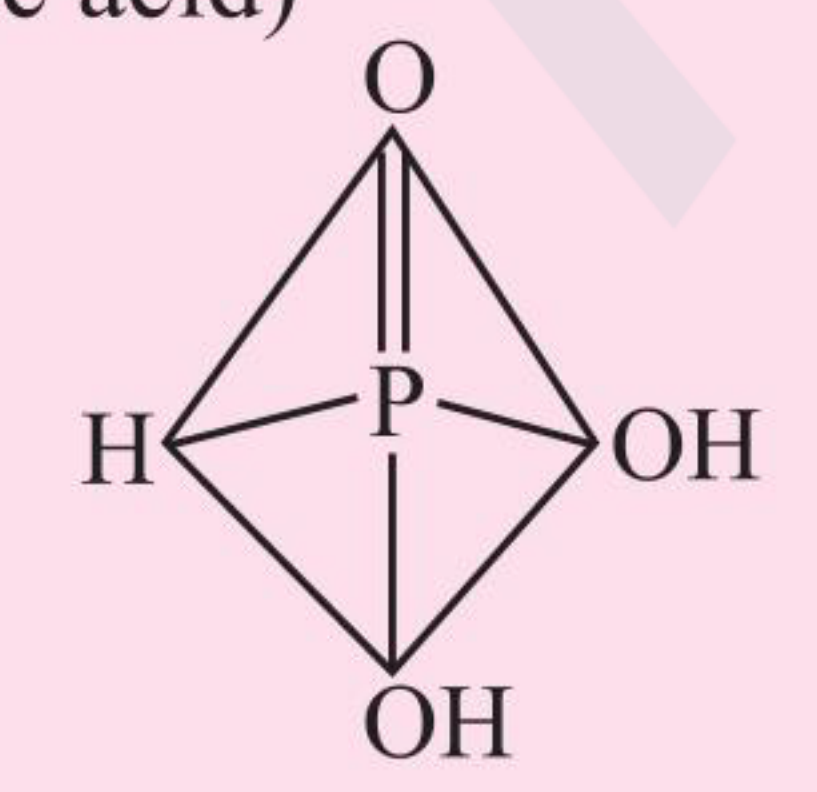
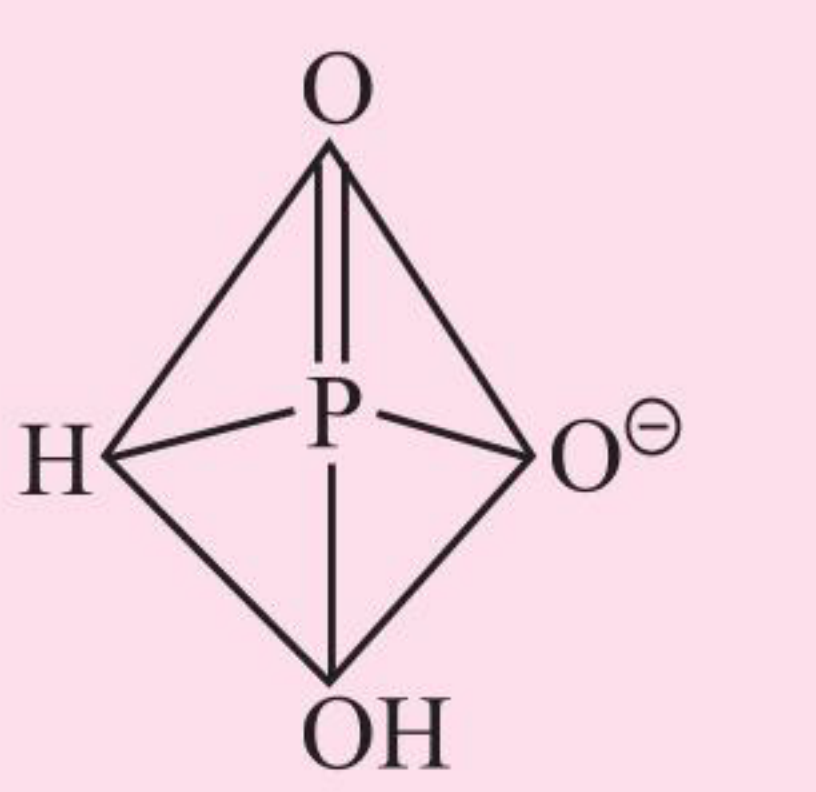
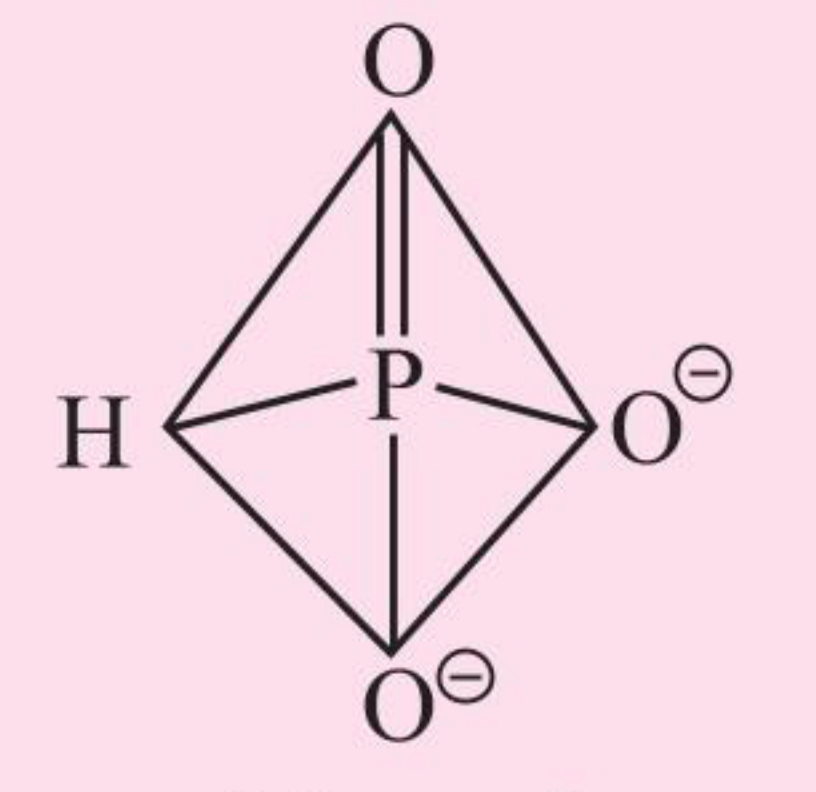
- d. P_4S_3 is used in matches. The head of the safety match box contains KClO_3 , KNO_2 or red lead along with grounded glass pieces and antimony sulphide. Sides of match box contain red phosphorous and sand powder.

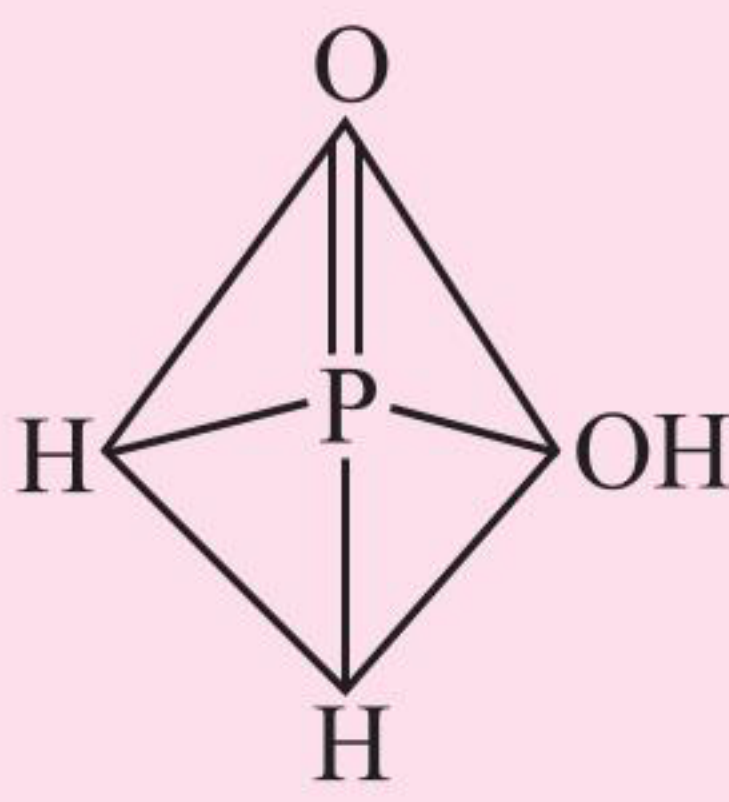
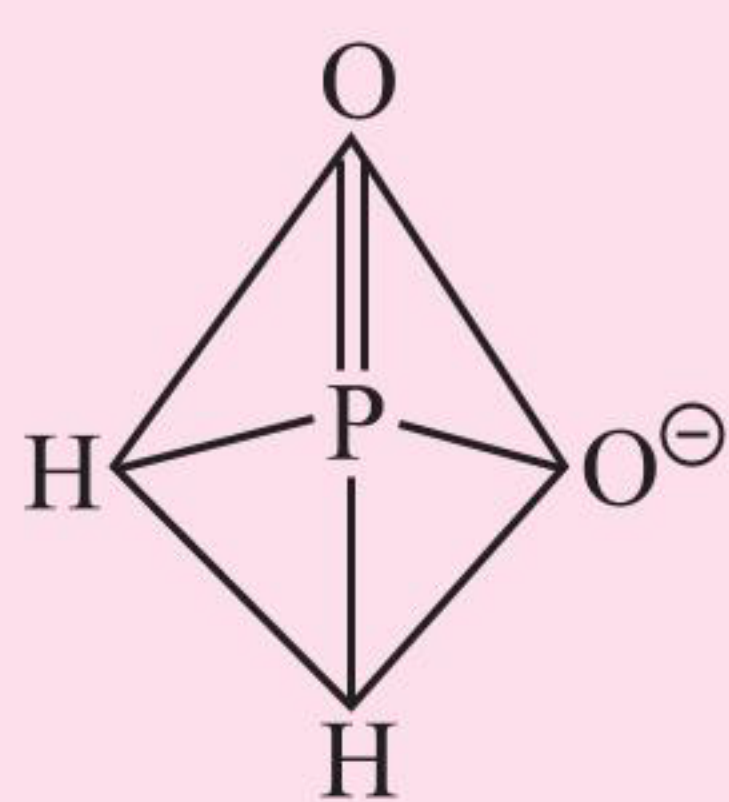
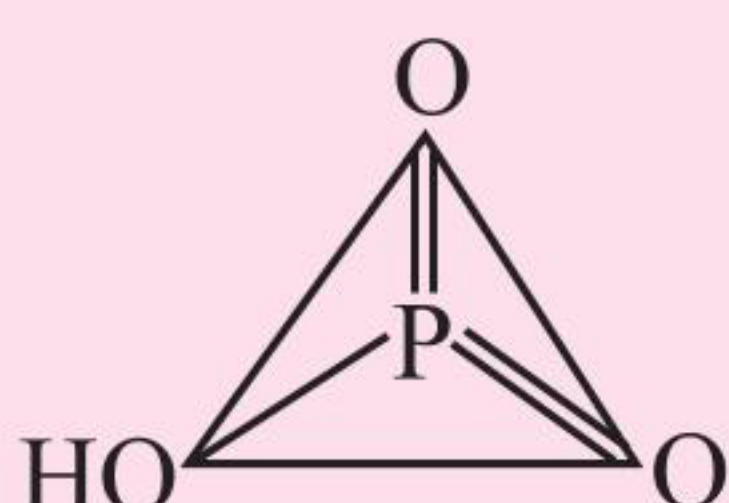
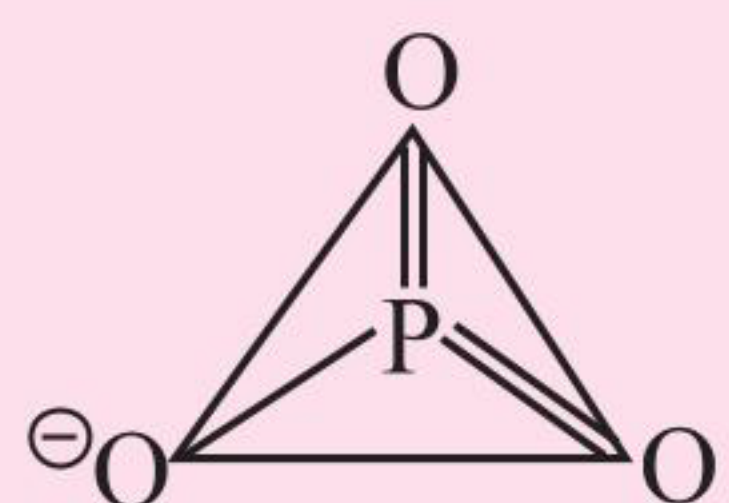
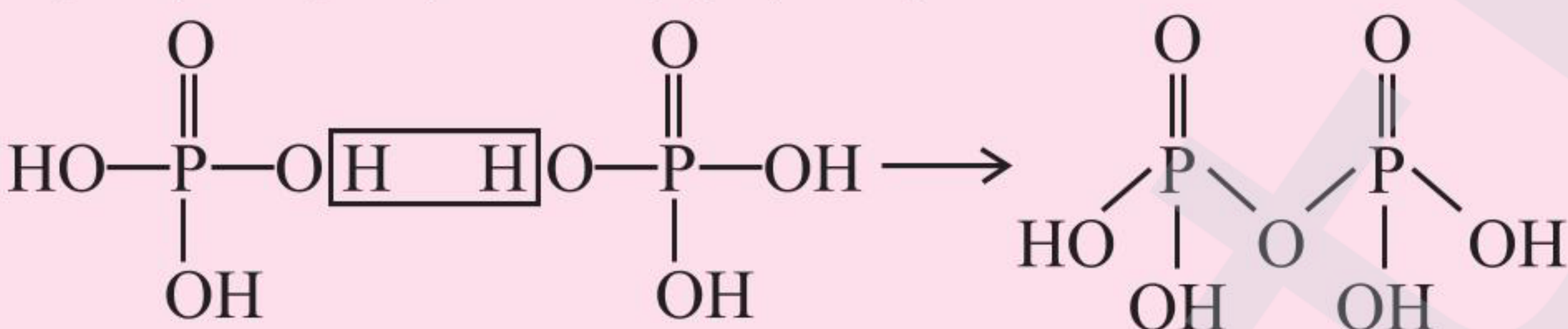
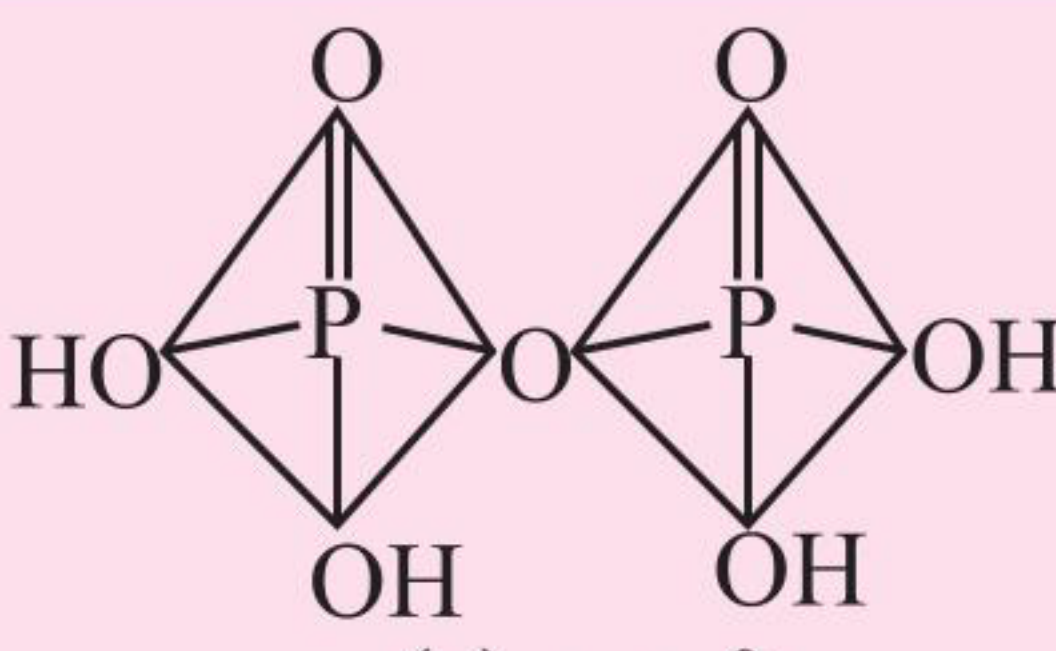
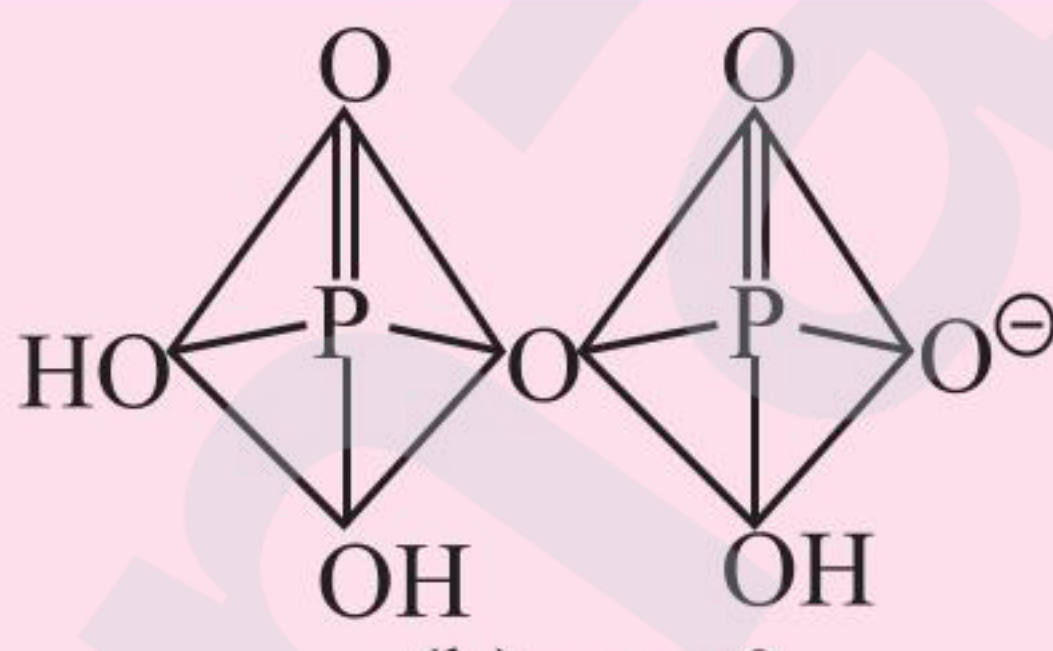
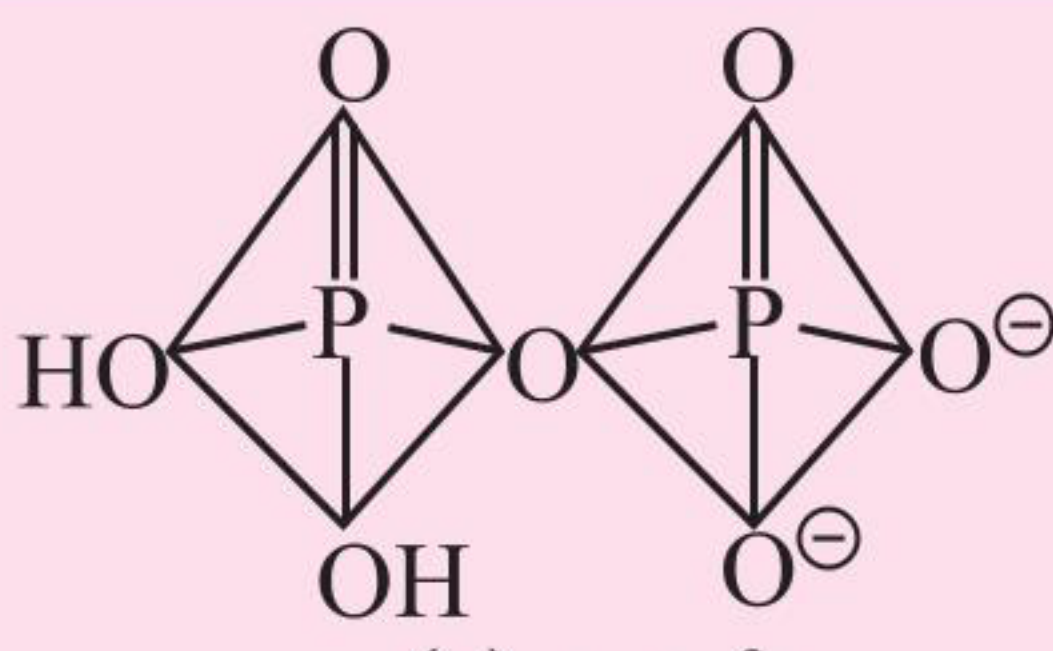
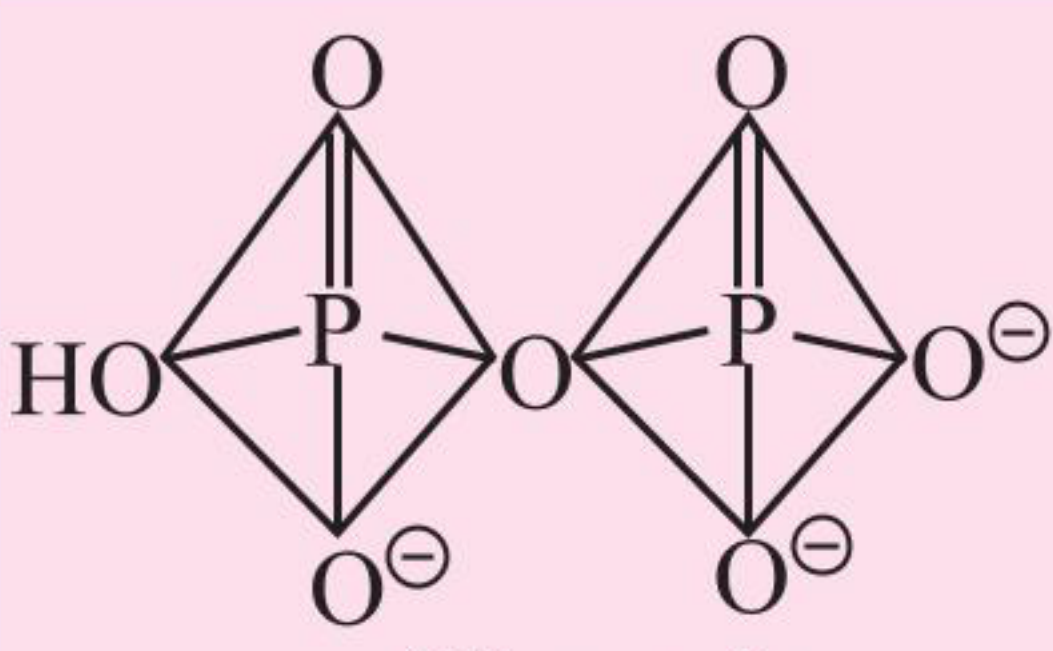
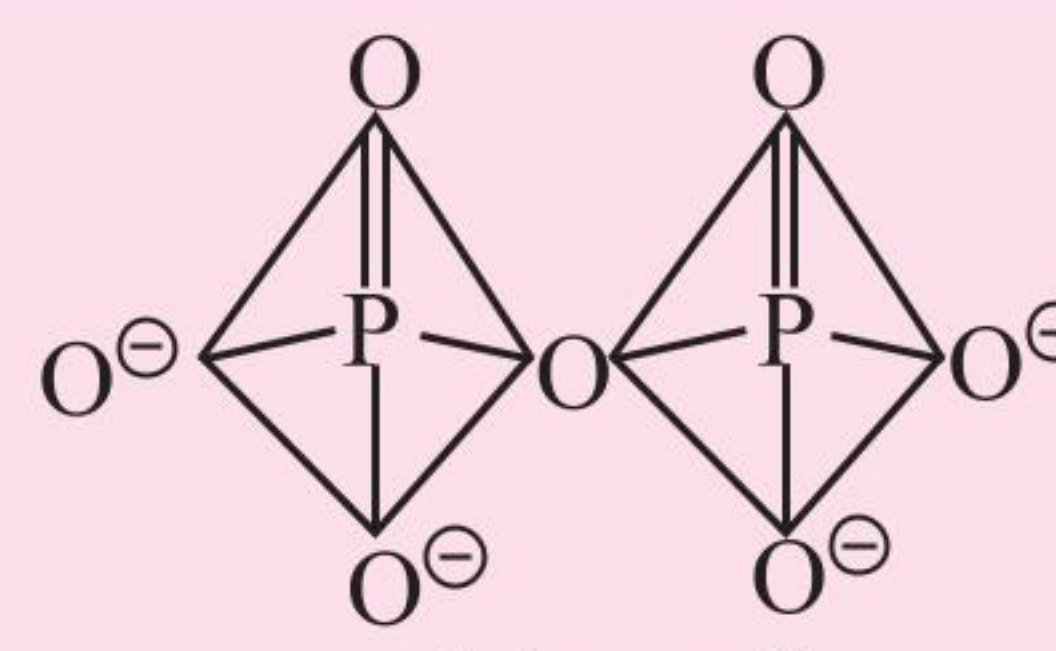
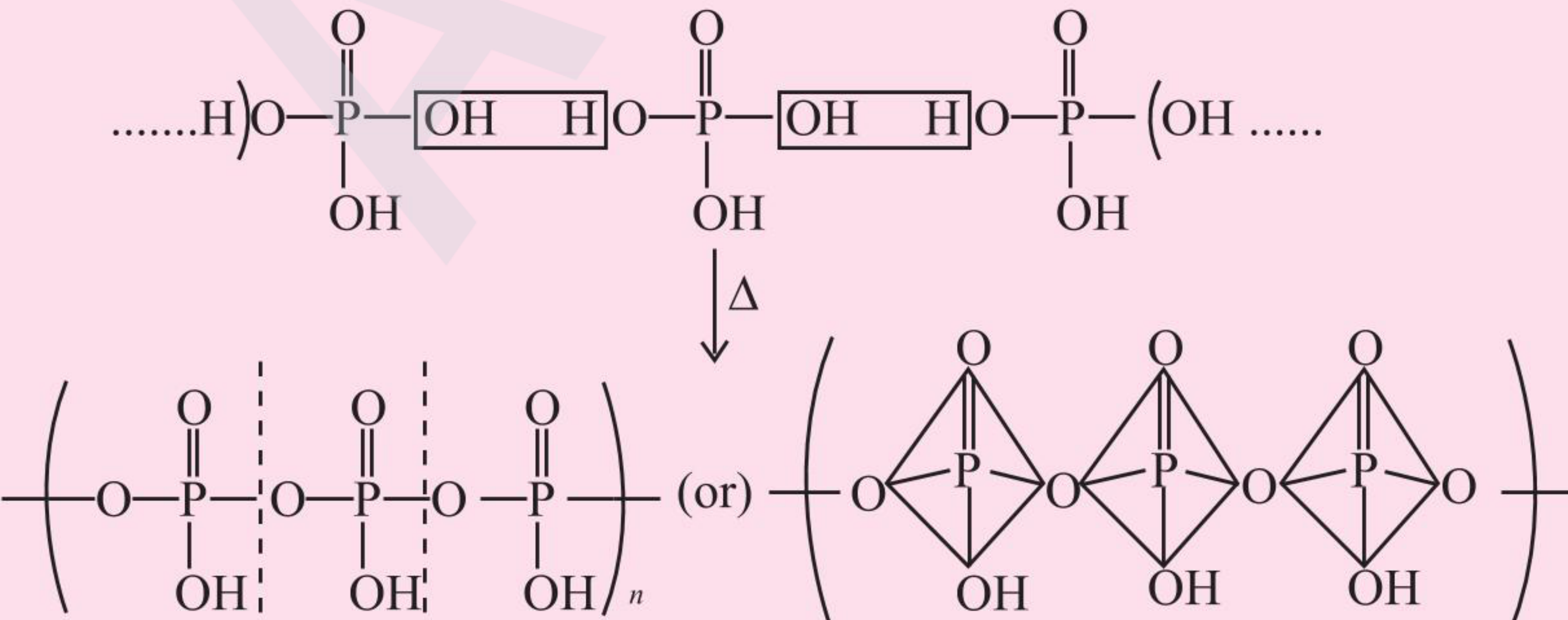
23. Some examples of hybridisation of group 15 ($5e^-$)

Symbols used: SN = Steric number, lp = lone pair, bp = bond pair, H = hybridisation, G = Geometry, S = Shape, T.H. = Tetrahedron, Tbp = Trigonal bipyramid, O.H. = Octahedral, Pbp = Pentagonal bipyramid, T.E. = Transition elements, C.N. = Coordination number, V = No. of valence e^- 's, M = No. of monovalent atom attached to central atom, O.S. = Oxidation state, (e) = equatorial bond, (a) = axial bond.

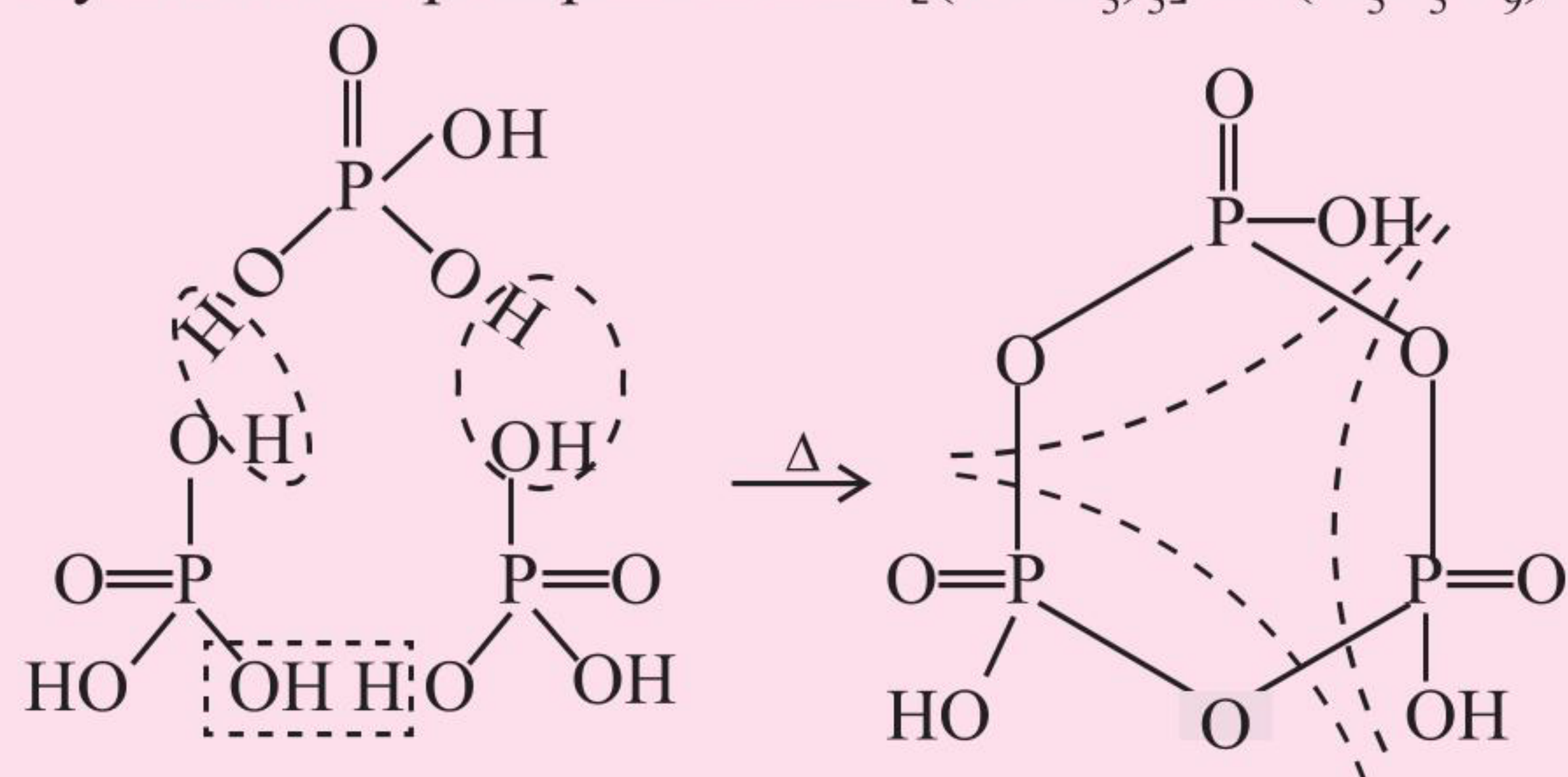
Note: Oxoacids and peroxyacids and their ions have same hybridisation, geometry and shape.

OXOACIDS OF PHOSPHOROUS

1.	H_3PO_4 (Tribasic acid) (O.S. = + 5) (Phosphoric acid) or (orthophosphoric acid)  (a) $\mu \neq 0$ (P — O) Bond order = 1.5 $H = \frac{1}{2} (V + M) = \frac{1}{2} (5 + 3) = 4$	H_2PO_4^- (Dihydrogen phosphate ion)  (b) $\mu \neq 0$ SN = 4 bp	HPO_4^{2-} (Hydrogen phosphate)  (c) $\mu \neq 0$ H = sp^3	PO_4^{3-} (Phosphate ion) [One (p π -d π) multiple bond]  (d) $\mu \neq 0$ Due to four equivalent resonance structures Geometry = T.H., 109° , $28'$
2.	H_3PO_5 (O.S. = + 5) (Peroxyphosphoric acid) or (Perphosphoric acid)  (a) $\mu \neq 0$ $H = \frac{1}{2} (V + M) = \frac{1}{2} (5 + 3) = 4$	H_2PO_5^- (Dihydrogen-peroxyphosphate ion)  (b) $\mu \neq 0$ SN = 4 bp	HPO_5^{2-} (Hydrogen-peroxy phosphate ion)  (c) $\mu \neq 0$ H = sp^3	PO_5^{3-} (Peroxyphosphate ion) [One (p π -d π) multiple bond]  (d) $\mu \neq 0$ Geometry = T.H., 109° , $28'$
3.	H_3PO_3 (Dibasic acid) (O.S. = +3) (Phosphorous acid) or (Phosphoric acid)  (a) $\mu \neq 0$ $H = \frac{1}{2} (V + M) = \frac{1}{2} (5 + 3) = 4$ (P — O) Bond order = 1.5	H_2PO_3^- (Dihydrogen phosphite ion)  (b) $\mu \neq 0$ SN = 4 bp	HPO_3^{2-} (Hydrogen phosphite ion)  (c) $\mu \neq 0$ H = sp^3	[One (p π -d π) multiple bond] Geometry = T.H., 109° , $28'$

4.	H_3PO_2 (Monobasic acid) (O.S. = +1) (Hypophosphorous acid) or (Phosphenic acid)	$\text{H}_2\text{PO}_2^\ominus$ (Dihydrogen hypophosphite ion)	[One (p π -d π) multiple bond]		
					
	(a) $\mu \neq 0$ $H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$ SN = 4 bp, H = sp^3 ,	(b) $\mu \neq 0$	G = T.H. $109^\circ, 28'$ (P — O) Band order = 1.5		
5.	HPO_3 (Monobasic acid) (O.S. = +5) (Metaphosphoric acid)	$\text{PO}_3^\ominus$ (Metaphosphate ion)	[One (p π -d π) multiple bond]		
					
	(a) $\mu \neq 0$	(b) (Due to three equivalent resonance structures) ($\mu = 0$)			
	$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 1) = 3$ SN = 3 bp, H = sp^2 ,	G = Planar 120°			
6.	Pyrophosphoric acid or diphosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$, tetrabasic acid, O.S. = +5 $\text{H}_3\text{PO}_4 + \text{H}_3\text{PO}_4 \xrightarrow{\Delta} \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$ 				
	$\text{H}_4\text{P}_2\text{O}_7$, Pyrophosphoric acid (a)	$\text{H}_3\text{P}_2\text{O}_7^\ominus$ Trihydrogen-pyrophosphate ion (b)	$\text{H}_2\text{P}_2\text{O}_7^{2-}$ Dihydrogen-pyrophosphate ion (c)	$\text{HP}_2\text{O}_7^{3-}$ Hydrogen-pyrophosphate ion (d)	$\text{P}_2\text{O}_7^{4-}$ Pyrophosphate ion (e)
	$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$ SN = 4 bp, H = sp^3 , Geometry = T.H., $109^\circ, 28'$, [2 (p π -d π) multiple bond]				
					
	(a) $\mu \neq 0$	(b) $\mu \neq 0$	(c) $\mu \neq 0$	(d) $\mu \neq 0$	(e) $\mu \neq 0$
7.	Polymetaphosphoric acid ($(\text{HPO}_3)_n$, Polybasic acid, O.S. = +5)  $\mu \neq 0$ [n (p π -d π) multiple bond] $H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$ SN = 4 bp, H = sp^3 , Geometry = T.H., $109^\circ, 28'$				

8. Cyclotrimeta phosphoric acid $[(\text{HPO}_3)_3]$ or $(\text{H}_3\text{P}_3\text{O}_9)$ (Tribasic acid, O.S. = +5)



$[3(\text{p}\pi\text{--d}\pi)$ multiple bond]

$\text{H}_3\text{P}_3\text{O}_9$,
Cyclotrimeta-
phosphoric acid

$\text{H}_2\text{P}_3\text{O}_9^\ominus$
Dihydrogen-
cyclotrimeta phos-
phate ion

$\text{HP}_3\text{O}_9^{2-}$
Hydrogen cyclotrimeta-
phosphate ion

$\text{P}_3\text{O}_9^{3-}$
Cyclotrimeta phosphate
ion

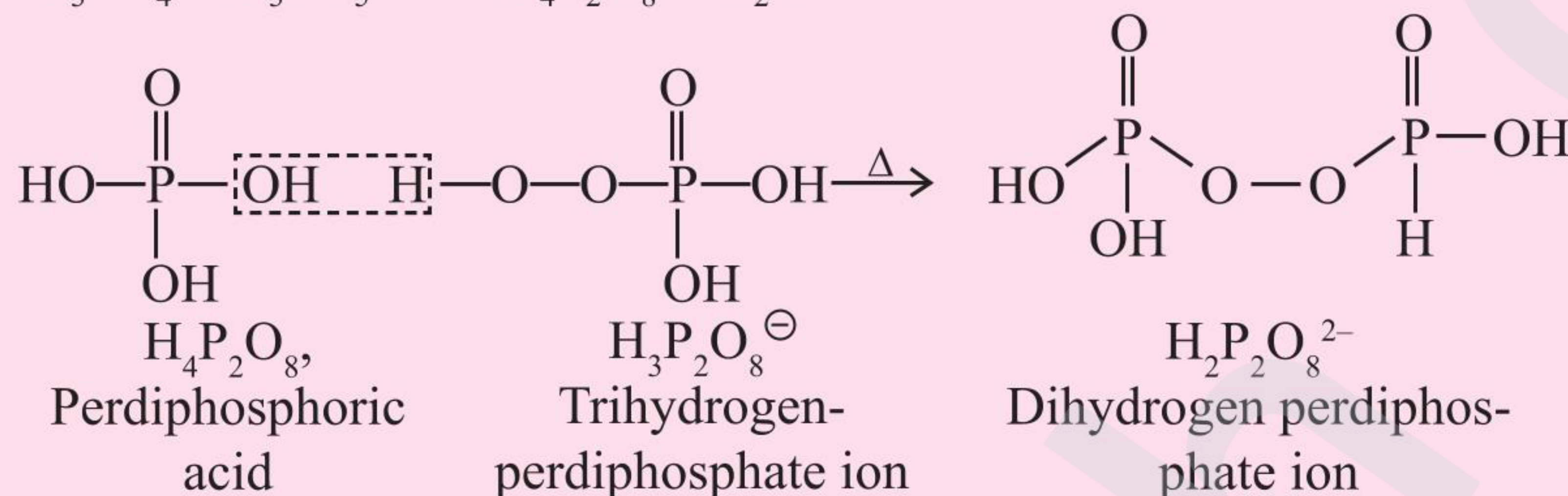
$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$$

SN = 4 bp,

$\text{H} = \text{sp}^3$,

Geometry = T.H., $109^\circ, 28'$

9. Perdiphosphoric acid or Peroxodiphosphoric acid $(\text{H}_4\text{P}_2\text{O}_8)$, Tetrabasic, O.S. = +5)



$2(\text{p}\pi\text{--d}\pi)$ multiple bond

$\text{H}_4\text{P}_2\text{O}_8$,
Perdiphosphoric
acid

$\text{H}_3\text{P}_2\text{O}_8^\ominus$
Trihydrogen-
perdiphosphate ion

$\text{H}_2\text{P}_2\text{O}_8^{2-}$
Dihydrogen perdipho-
sphate ion

$\text{HP}_2\text{O}_8^{3-}$
Hydrogen peridipho-
sphate ion

$\text{P}_2\text{O}_8^{4-}$
Perdiphosphate ion

$$H = \frac{1}{2}(V + M) = \frac{1}{2}(5 + 3) = 4$$

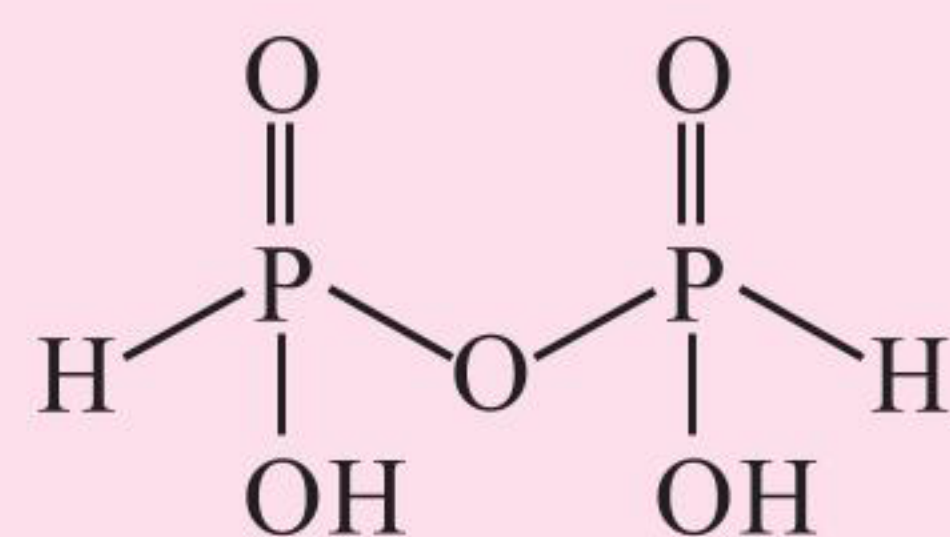
SN = 4 bp,

$\text{H} = \text{sp}^3$,

Geometry = T.H., $109^\circ, 28'$

10. Pyrophosphorous acid $(\text{H}_4\text{P}_2\text{O}_5)$ (Dibasic, O.S. = +3)

$2(\text{p}\pi\text{--d}\pi)$ multiple bond



$\text{H}_3\text{P}_2\text{O}_5^\ominus$
Trihydroxypro-
phosphite ion

$\text{H}_2\text{P}_2\text{O}_5^{2-}$
Dihydroxypro-
phosphite ion

$$H = \frac{1}{2}(V + M) = (5 + 3) = 4$$

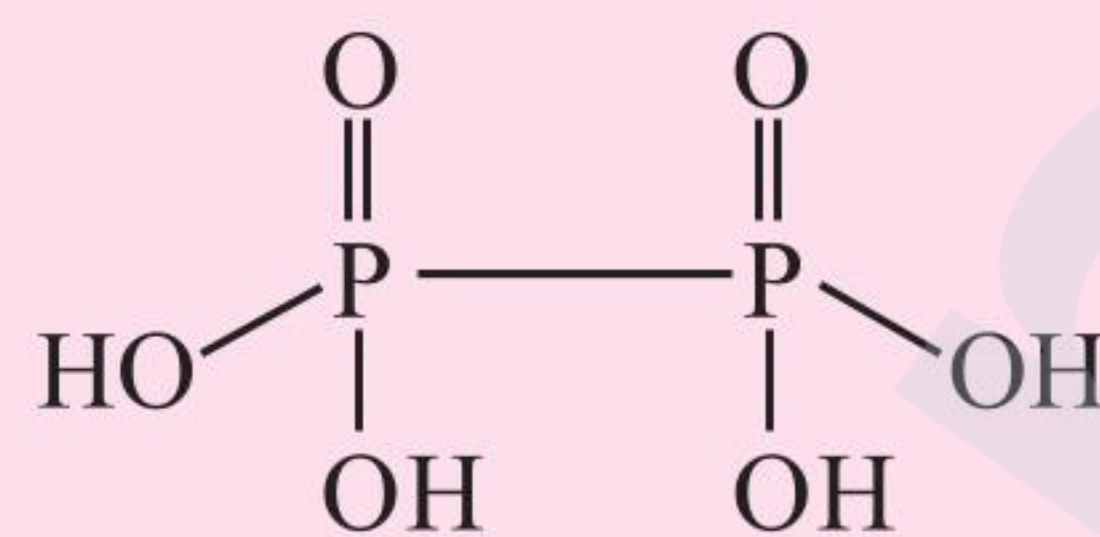
SN = 4 bp,

$\text{H} = \text{sp}^3$,

Geometry = T.H.,

11. Hypophosphoric acid $(\text{H}_4\text{P}_2\text{O}_6)$ (Tetrabasic, O.S. = +4)

$2(\text{p}\pi\text{--d}\pi)$ multiple bond



$\text{H}_3\text{P}_2\text{O}_6^\ominus$
Trihydroxyphos-
phate ion

$\text{H}_2\text{P}_2\text{O}_6^{2-}$
Dihydroxyphos-
phate ion

$\text{HP}_2\text{O}_6^{3-}$
Hydroxyphos-
phate ion

$\text{P}_2\text{O}_6^{4-}$
Hypophosphate ion

$$H = \frac{1}{2}(V + M) = (5 + 3) = 4$$

(P—O) bond order = 1.5

SN = 4 bp,

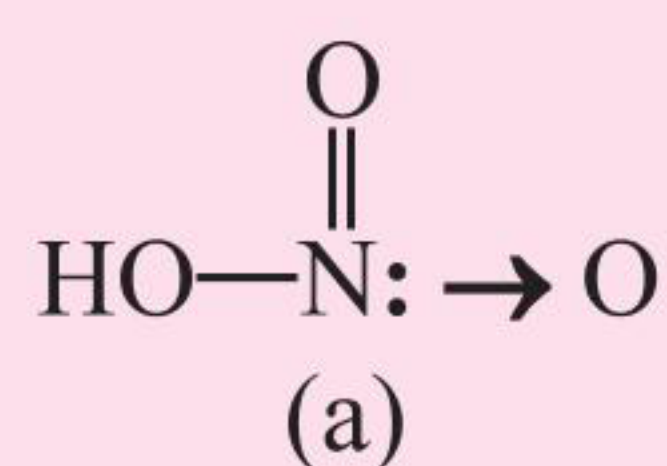
$\text{H} = \text{sp}^3$,

Geometry = T.H.

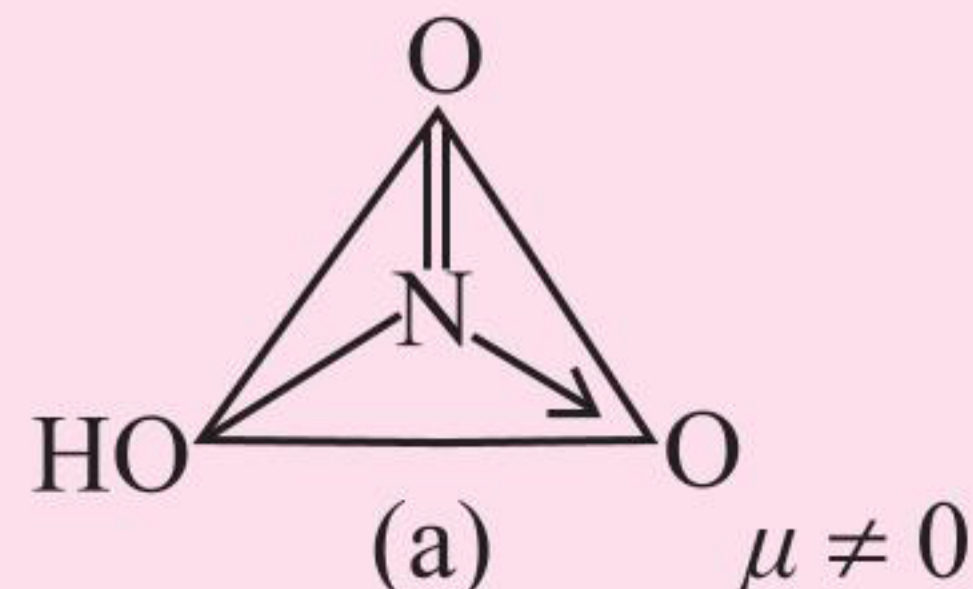
12. HNO_3 (nitric acid, monobasic, O.S. = +5)

$\text{NO}_3^\ominus$ nitrate ion
(or)

N atom does not have
d-orbitals. So $[\text{one } (\text{p}\pi\text{--p}\pi) \text{ multiple bond}]$

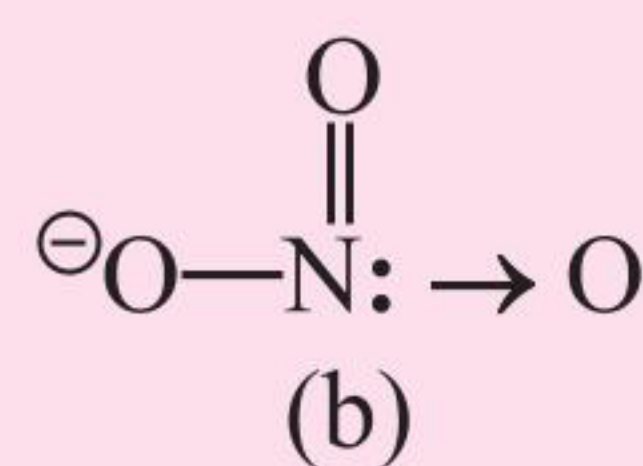


(a)

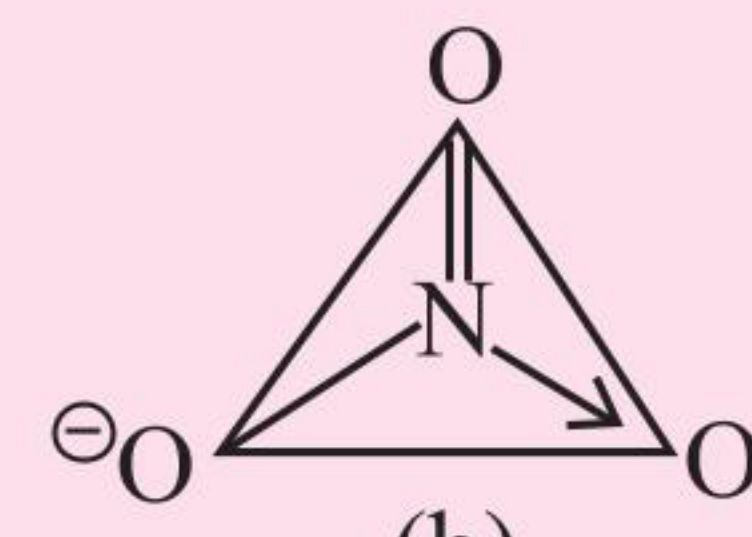


(a)

$\mu \neq 0$



(b)



(b)

$\mu \neq 0$

$$H = \frac{1}{2}(V + M) = (5 + 1) = 3$$

SN = 3 bp,

$\text{H} = \text{sp}^2$,

Geometry = Planar 120°

13. HNO_3 does not form per-oxy acid because its peroxy form having two central atom is not possible.

14. HNO_2 (Nitrous acid, monobasic, O.S. = + 3)

HNO_2 ,
Nitrous acid (or)

$\text{HO}-\text{N}(\text{O})$
(a)

$\text{H} = \frac{1}{2} (V + M) = (5 + 1) = 3$

$\text{NO}_2^\ominus$
Nitrite ion

$^\ominus\text{O}-\text{N}(\text{O})$
(b)

$\text{H} = sp^2$

[One (p π -p π) multiple bond]

$\text{O}^\ominus-\text{N}(\text{O})-\text{O}$
(b)

Geometry = Planar, Shape = Bent or V shape

15. Hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$, Dibasic, O.S. = + 1)

$\text{HO}-\ddot{\text{N}}=\ddot{\text{N}}-\text{OH}$
Hyponitrous acid
(a)

$\text{H} = \frac{1}{2} (V + M) = \frac{1}{2} (5 + 1) = 3$

$\text{HO}-\ddot{\text{N}}=\ddot{\text{N}}-\text{O}^\ominus$
Hydrogen hyponitrite ion
(b)

$\text{SN} = 2 \text{ bp} + 1 \text{ lp} = 3$

$\text{O}^\ominus-\ddot{\text{N}}=\ddot{\text{N}}-\text{O}^\ominus$
Hyponitrite ion
(c)

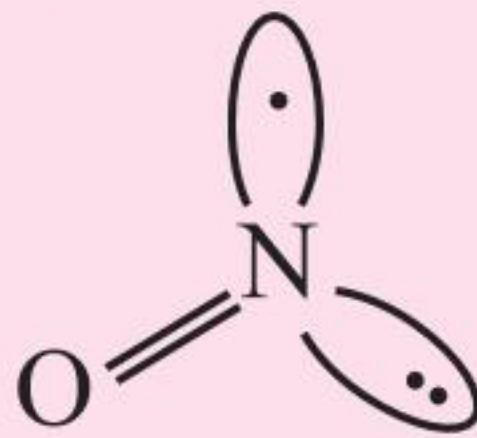
$\text{H} = sp^2$, G = planar Shape = Bent or shape

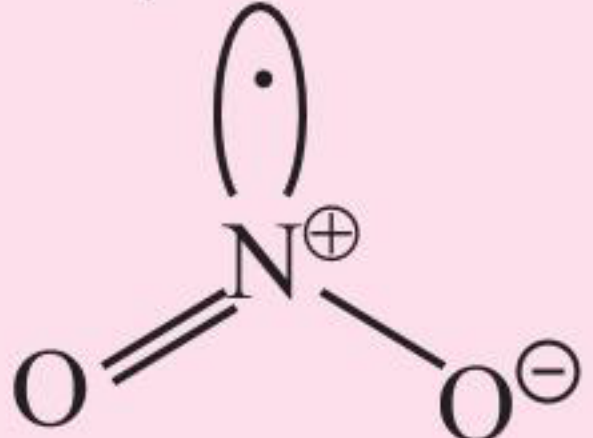
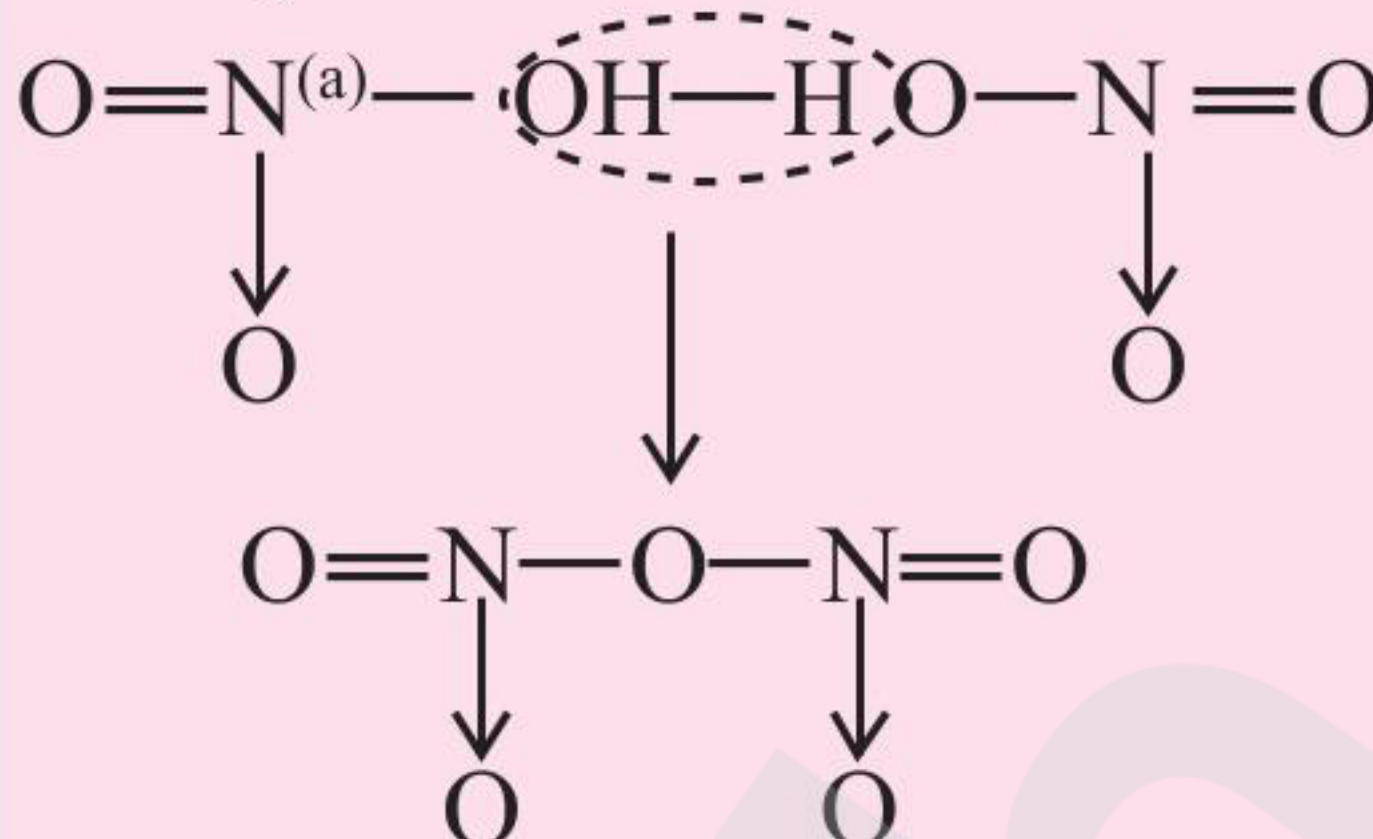
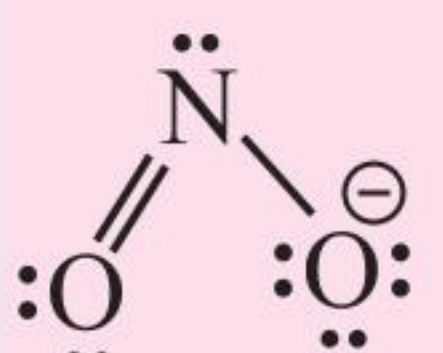
[One (p π -p π) multiple bond]

It shows tautomerism

$\text{HO}-\ddot{\text{N}}=\ddot{\text{N}}-\text{OH} \rightleftharpoons \text{HO}-\ddot{\text{N}}=\text{N}^+=\text{OH} \rightleftharpoons \text{HO}-\ddot{\text{N}}\text{H}=\text{N}=\text{O}$

24. Oxides of Nitrogen and their ions:
(Note: π bond is excluded in bond pair i.e., from hybridisation.)

S. No.	Oxides of nitrogen and O.S. of N	Characteristics	SN	Hyb. (H)	Geometry and shape, (G and S) and dipole moment
1.	Nitrous oxide or laughing gas (N_2O) (O.S. = +1) $:\text{N}^a \equiv \text{N}^b \rightarrow \ddot{\text{O}}:$ or $:\text{N}^a \equiv \text{N}^b \rightarrow \text{O}^\ominus$ ↑ one bond pair	Neutral and diamagnetic 2(p π -p π) multiple bonds	SN at $\text{N}^a = 1 \text{ bp} + 1 \text{ lp} = 2$ SN at $\text{N}^b = 2 \text{ bp} = 2$	sp	G = Linear $\mu \neq 0$
2.	Nitric oxide $\cdot\ddot{\text{N}}=\text{O}$ (O.S. = +2)	Neutral and paramagnetic (p π -p π) multiple bonds	SN = 1 bp + 1 lp + 1 odd electrons = 3 $\text{H} = \frac{1}{2} (V + M + \text{odd electrons})$ $= \frac{1}{2} (5 + 0 + 1) = 3$	sp^2	G = Planar Shape = Linear  $\mu \neq 0$
3.	Dinitrogen trioxide (N_2O_3) (O.S. = + 3) $\text{O}=\text{N}^{(a)}-\text{N}^{(b)}=\text{O}$ ↓ O or $\text{O}=\text{N}^{(a)}-\text{N}^{(b)}=\text{O}$ ↓ $\text{O}^\ominus$	Acidic and diamagnetic 2(p π -p π) multiple bonds	SN at $\text{N}^a = 3 \text{ bp}$ SN at $\text{N}^b = 2 \text{ bp} + 1 \text{ lp} = 3$ $\text{H} = \frac{1}{2} (V + M)$ rule is not applicable in this case.	sp^2	G at N^a = Planar G at N^b = Planar Shape at N^b = Bent $\mu \neq 0$

4.	Nitrogen dioxide (NO_2) (O.S. = +4) $\text{O} \leftarrow \text{N}=\text{O}$ (OR) $\text{O}^{\ominus}-\text{N}^{\oplus}=\text{O}$	Acidic and paramagnetic one ($\text{p}\pi\text{-p}\pi$) multiple bonds	$\text{SN} = 2\text{bp} + 1 \text{ odd electron} = 3$ $H = \frac{1}{2}(V+M) + 1 \text{ odd electron}$ $= \frac{1}{2}(5 + 0 + 1) = 3$	sp^2	G = Planar, Shape = Bent $\mu \neq 0$  Expected bond angle = 120° but observed bond angle = 134°
5.	Dinitrogen tetroxide (N_2O_4) (O.S. = +4) $\text{O}=\text{N}^{(a)}-\text{N}^{(b)}=\text{O}$ $\downarrow \quad \downarrow$ $\text{O} \quad \text{O}$ (OR) $\text{O}=\text{N}^{\oplus}-\text{N}^{\oplus}=\text{O}$ $\downarrow \quad \downarrow$ $\text{O}^{\ominus} \quad \text{O}^{\ominus}$	Acidic and diamagnetic 2($\text{p}\pi\text{-p}\pi$) multiple bonds	Same SN at N^a or N^b. $\text{SN} = 3 \text{ bp} = 3$ $H = \frac{1}{2}[(V+M \pm \text{charge})]$ rule is not applicable in this case.	sp^2	G = Planar $\mu \neq 0$
6.	Dinitrogen pentaoxide (N_2O_5) (O.S. = +5) $\text{O}=\text{N}^{(a)}-\text{O}-\text{N}^{(b)}=\text{O}$ $\downarrow \quad \downarrow$ $\text{O} \quad \text{O}$ (OR) $\text{O}=\text{N}^{\oplus}-\text{O}-\text{N}^{\oplus}=\text{O}$ $\downarrow \quad \downarrow$ $\text{O}^{\ominus} \quad \text{O}^{\ominus}$	Acidic and anhydride of HNO_3 , i.e.  2 ($\text{p}\pi\text{-p}\pi$) multiple bond	Same SN at N^a or N^b. $\text{SN} = 3 \text{ bp} = 3$ $H = \frac{1}{2}[(V+M \pm \text{charge})]$ rule is not applicable in this case.	sp^2	G = Planar $\mu \neq 0$
7.	$\text{NO}_2^{\oplus}$ (O.S. = +5) $:\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:$ $\uparrow \quad \uparrow$ 2 bond pairs (π bonds are excluded from hybridisation)	Acidic and diamagnetic 2 ($\text{p}\pi\text{-p}\pi$) multiple bond	$\text{SN} = 2 \text{ bp} = 2$ $H = \frac{1}{2}[V+M - (+\text{ve charge})]$ $= \frac{1}{2}(5 + 0 - 1) = 2$	sp	G = Planar Bond angle = 180° $\mu = 0$
8.	$\text{NO}_2^{\ominus}$ (O.S. = +3) Nitrite ion 	Acidic and diamagnetic one ($\text{p}\pi\text{-p}\pi$) multiple bond	$\text{SN} = 2 \text{ bp} + 1 \text{ lp} = 3$ $H =$ $\frac{1}{2}[V+M + \text{No. of } -\text{ve charge}]$ $= \frac{1}{2}(5 + 0 - 1) = 3$	sp^2	G = Planar Shape = Bent $\mu \neq 0$ Expected bond angle = 120° But observed bond angle = 115°
9.	$\text{NO}_3^{\ominus}$ (O.S. = +5) Nitrite ion $\text{O}=\text{N}-\text{O}^{\ominus}$ $\parallel$ O	Acidic and diamagnetic 2 ($\text{p}\pi\text{-p}\pi$) multiple bond	$\text{SN} = 3 \text{ bp} = 3$ $H =$ $\frac{1}{2}[V+M + \text{No. of } -\text{ve charge}]$ $= \frac{1}{2}(5 + 0 + 1) = 3$	sp^2	G = Planar $\mu = 0$ Bond angle = 120°
10.	$\text{N}_3^{\ominus}$ (Azide ion)	The possible linear structures are shown as: $[\text{:}\ddot{\text{N}}=\text{N}=\ddot{\text{N}}:]^{\ominus}$ (a) $[\text{:}\ddot{\text{N}}-\text{N}\equiv\text{N}:]^{\ominus}$ (b) $[\text{:}\text{N}\equiv\text{N}-\ddot{\text{N}}:]^{\ominus}$ (c) SN on the central N atom in all structures = 2 bp, $H = sp$, Geometry = linear			

2.1 INTRODUCTION

Group 15 of the periodic table comprises nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb) and bismuth (Bi). These elements are collectively known as **pnictogen** and their compounds as **pniconides**. The name **pnictogen** is derived from the Greek word **pnicomigs** which means suffocation. Pniconides contain E³⁻ species.

These are *p*-block elements as the last differentiating element is accommodated in *np* orbitals

2.2 OCCURRENCE

Molecular nitrogen comprises 78% (by volume) of the earth atmosphere, but it is not very abundant in the earth crust. Nitrogen is the thirty-third most abundant element by mass in the earth crust.

Nitrogen mainly occurs as nitrates i.e. chile saltpetre (NaNO₃) and Indian saltpetre (KNO₃). Nitrogen is an essential constituent of proteins and amino-acids. Nitrates and other nitrogen compounds are extensively used in fertilisers and explosives. Phosphorous is the eleventh most abundant element in the earth crust. It is highly reactive and does not occur free in nature. It occurs in minerals of the apatite family, Ca₉(PO₄)₆·CaX₂ (X = F, Cl or OH) i.e. fluorapatite, Ca₉(PO₄)₆·CaF₂, chlorapatite, Ca₉(PO₄)₆·CaCl₂ or hydroxyapatite, Ca₉(PO₄)₆·Ca(OH)₂. These are main components of phosphate rocks. Phosphorous is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. It also occurs in nucleic acids, i.e. DNA and RNA which control the hereditary effects in human beings and in adenosine triphosphate (ATP) and adenosine diphosphate (ADP) which are of vital importance for the production of energy in cells.

The elements As, Sb and Bi are not very abundant. Their most important source is as sulphides occurring as traces in other ores. The only common ores of arsenic are:

- 1. Arsenopyrites – FeAsS
- 2. Realgar – As₄S₄
- 3. Orpiment – As₂S₃

The most important ore of antimony is stibnite, Sb₂S₃. Bismuth occurs as bismuthinite (Bi₂S₃) and bismite (Bi₂O₃).

2.3 ATOMIC AND PHYSICAL PROPERTIES

Some of the important atomic and physical properties of group 15 elements along with their electronic configurations are given in Table 2.1.

2.3.1 ELECTRONIC CONFIGURATION

The general valence shell electronic configuration of group 15 is *ns²np³* (where *n* = 2 to 6). The three electrons in the *np* orbitals are distributed as *np_x¹ np_y¹ np_z¹* in accordance with Hund’s rule.

The *ns* orbital in group 15 elements is completely filled and *np* orbitals are half filled, making their electronic configuration extra stable.

2.3.2 ATOMIC AND IONIC RADII

- 1. Down the group (↓), i.e. from N to Bi, the covalent (atomic) and ionic radii (in a particular oxidation state) increases. There is considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed.

Explanation: Down the group (↓), i.e. from N to Bi, with addition of a new principal energy shell in each succeeding element, effective nuclear charge decreases and covalent radii increases. But the increase in radii at each step is not the same due to difference in electronic configuration of N and P on one hand and As, Sb and Bi on other hand. In N and P, the valence shell electrons are preceded by noble gas core, hence shielding effect is very high and thus decrease in effective nuclear charge is high and there is considerable increase in radii from N to P. But in As, Sb and Bi, in between the valence shell electrons and noble gas core lesser shielding fully filled *d* and/or *f* orbitals are present. Thus shielding effect is less and effective nuclear charge increases which reduces the effect of addition of a new energy shell to some extent. Hence from As to Bi, increase in covalent radii is very less.

Table 2.1 Atomic and physical properties of Group 15 element

Elements	Nitrogen	Phosphorous	Arsenic	Antimony	Bismuth
Symbol	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass/(g mol ⁻¹)	14.01	30.97	74.92	121.75	208.98
Electronic configuration	[He] 2s ² 2p ³	[Ne] 3s ² 3p ³	[Ar] 3d ¹⁰ 4s ² 4p ³	[Kr] 4d ¹⁰ 5s ² 5p ³	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Ionisation enthalpy/(kJ mol ⁻¹)	I	1402	1012	834	703
	II	2856	1798	1595	1610
	III	4577	2910	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius/(pm) ^a	70	110	121	141	148
Ionic radius/(pm)	171 ^b	212 ^b	222 ^b	76 ^c	103 ^c
Melting point / (K)	63 ^d	317 ^e	1089 ^f	904	544
Boiling point/(K)	772 ^d	554 ^e	888 ^g	1860	1837
Density at 298 K/(g cm ⁻³)	0.879 ^h	1.823	5.778 ⁱ	6.697	9.808

^aE^{III} single bond (E = element); ^bE³⁻; ^cE³⁺; ^dMolecular nitrogen; ^ewhite phosphorous; ^fGrey (α-form) at 38.6 atm; ^gsublimation temperature; ^hat 63 K; ⁱGrey α-form.

2. The atomic radii of elements of group 15 are less than the corresponding elements of group 14.

Explanation: From left to right ($\rightarrow$) i.e. from group 14 to 15 in a given period, with increase in nuclear charge, the electron is added in the same shell. Consequently, the effective nuclear charge increases and covalent radii decreases.

e.g. atomic or covalent radii of N is less than carbon.

2.3.3 IONISATION ENTHALPY (IE or $\Delta_f H^\ominus$)

The ionisation enthalpies of the elements of group 15 are much higher than the corresponding elements of group 14. Down the group ($\downarrow$) the values of the ionisation energies decrease.

Explanation: Because of increased nuclear charge, reduced atomic radii and stable half-filled configurations, they have much less tendency to lose electrons as they are more tightly held by the nucleus. Consequently the ionisation enthalpies of group 15 elements are much higher as compared to elements of group 14 carbon family. The decrease in their values, down the group is due to gradual increase in the atomic size which reduces the force of attraction on the electrons by the nucleus.

IE: $N > P > As > Sb > Bi$

2.3.4 ELECTRONEGATIVITY (EN)

Group 15 elements are more electronegative than group 14 elements. Electronegativity of elements of group 15 shows a gradual decrease down the group from N to Bi.

Explanation: As the elements of group 15 have smaller atomic size and need less number of electrons to attain noble gas configuration as compared to elements of group 14, they are more electronegative. Down the group, due to the gradual increase in the atomic size, attraction by the nucleus for the electrons decreases. Hence their electronegativity values decrease down the group.

EN: $N > P > As > Sb > Bi$

2.3.5 MELTING AND BOILING POINTS

The melting points of group 15 elements first increase from nitrogen to arsenic and then decrease to antimony and bismuth. The melting points of antimony and bismuth are less than the expected values. The boiling points, however, increase regularly from N to Bi.

Explanation: The melting points increase down the group due to increase in their atomic size. The unexpected decrease in the melting points of antimony and bismuth is because of their tendency to form three covalent bonds instead of five covalent bonds due to **inert pair effect**. This results in weakening the attraction among their atoms thus lowering their melting points. Because of larger size of atoms, bismuth has still weaker interatomic forces than antimony and thus has lower melting points.

Melting points: $N < P < Bi < Sb < As$

Down the group ($\downarrow$), i.e. from N to Bi, boiling points increase due to an increase in their atomic size (exception $P < N$).

Boiling points: $P < N < As < Bi < Sb$

2.3.6 DENSITY

The density of the element of group 15 increases regularly from N to Bi as usual.

2.3.7 METALLIC CHARACTER

Metallic character increases down the group ($\downarrow$) from N to Bi.

Explanation: Down the group, the atomic size increases and the outer electrons get farther from the nucleus. The ionisation energy decreases and the electrons become more loosely held and have a tendency to be lost readily. Thus the metallic character increases. First two elements of this group (N and P) are non-metals, the next two (As and Sb) are metalloids, while Bi is a typical metal. Thus the metallic character increases from N to Bi.



The elements of group 15 are less metallic than the corresponding elements of group 14. This is due to increase in nuclear charge and electronegativity from group 14 to group 15, hence the metallic character decreases from group 14 to 15.

2.3.8 ATOMIC AND PHYSICAL STATE

Nitrogen exists as diatomic gaseous molecule, phosphorous, arsenic and antimony exist as discrete tetrahedra tetraatomic solid molecules and bismuth is metallic at ordinary temperature.

2.3.9 $p\pi-p\pi$ MULTIPLE BOND

Nitrogen because of its small size and high electronegativity forms **$p\pi-p\pi$ multiple** bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Thus, nitrogen exists as a diatomic molecule with a triple bond ($N \equiv N$, one σ - and two π - bonds) between the two atoms. These N_2 molecules are held together by weak **van der Waals** forces of attraction which can be easily broken by the collisions of the molecules at room temperature. Therefore, N_2 is a gas at room temperature. Since bond dissociation enthalpy ($941.4 \text{ kJ mol}^{-1}$) of $N \equiv N$ molecule is very high. N_2 is an inert gas.

The other elements of group 15 do not form **$p\pi-p\pi$ multiple** bonds since their atomic orbitals are large and diffused that they cannot have effective overlapping. Thus, P, As and Sb do not form **$p\pi-p\pi$ multiple** bonds. Instead they prefer to form single bonds as $P-P$, $As-As$ and $Sb-Sb$ while Bi forms metallic bonds in the elemental state. Actually, phosphorus, arsenic and antimony exist as discrete tetraatomic tetrahedral molecules such as P_4 , As_4 , Sb_4 , etc. containing $E-E$ single bonds.

Due to bigger size, the forces of attraction holding the tetraatomic molecules of P_4 , As_4 , Sb_4 , etc. are quite strong and hence cannot be broken by the collisions of the molecules at room temperature. Therefore, P_4 , As_4 , Sb_4 all are solids at room temperature.

2.3.10 CATENATION

The elements of group 15 also show the property of catenation (self-linking of atoms) but to a much smaller extent than elements of group 14. The reason being that the $E-E$ bond strength of these elements is much lower than that of $C-C$ bond.

Bond	C—C	N—N	P—P	As—As
Bond strength (kJ mol^{-1})	347	159	213	1474

Among the elements of group 15, phosphorus has the maximum tendency for catenation forming cyclic as well open chain compounds consisting of many phosphorus atoms.

Nitrogen has little tendency for catenation since N—N single bond is very weak due to large interelectronic repulsions between the lone pairs of electrons present on the N-atoms of N—N bond having small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of *d* orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form ***d*π–*d*π bond** as the heavier elements can e.g., $R_3P=O$ or $R_3P=CH_2$ (*R* = alkyl group). Phosphorus and arsenic can form ***d*π–*d*π bond** also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

Nitrogen can form chains containing up to three N-atoms, e.g., hydrazoic acid, N_3H or azide ion, $N_3^\ominus$ ion. Due to decrease in E—E bond strength down the group, catenating ability decreases from P to As. As can form a chain of only two atoms.

2.4 CHEMICAL PROPERTIES

2.4.1 OXIDATION STATES

The elements of group 15 have $ns^2 np^3$ as their valence shell electronic configuration. They can complete their octets in two different ways:

- 1. Electron transfer:** The atoms of the elements of this group may accept three electrons from more metallic elements to form triply charged negative ions such as nitride, N^{3-} ion and phosphide, P^{3-} ion and thereby attain noble gas configuration. Only small atoms can form highly charged negative ions because of their greater electronegativities. Obviously nitrogen with greater electronegativity and smaller size, has a stronger tendency to form triply charged negative ions and this tendency decreases down the group because of increase of size and decrease in electronegativity.

The elements of this group also exhibit +3 and +5 oxidation states. The +5 ions are generally not known because their sizes will be very small and their ionisation energy will be very high. Down the group, the stability of +3 oxidation state increases while that of +5 decreases. This is due to **inert pair effect** as ns^2 electrons tend to remain paired in heavier *p*-block elements i.e., they do not take part in the bond formation. It is due to the fact that *s*-electrons are penetrating in the preceding shell in such a way that they are a part of inner shell electrons and are, therefore, removed with difficulty.

Bi^{3+} and Sb^{3+} are stable due to decrease in IE. BiF_3 is known, but BiF_5 is not.

Besides –3, N and P also show oxidation states of –2 in hydrazine (NH_2NH_2) and diphosphine (PH_2PH_2) respectively. Nitrogen also shows an oxidation state –1 in hydroxylamine (NH_2OH) but phosphorous does not. In case of nitrogen, all O.S. from +1 to +4 tend to disproportionate in acid solution. For example,

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$$

- 2. Electron sharing:** Since the atoms of these elements contain three unpaired *p*-electrons so these can pair with unpaired electrons in another atom or atoms to form covalent bonds e.g., NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 .

2.4.2 MAXIMUM COVALENCY

Since nitrogen does not possess any vacant *d*-orbitals in its valence shell ($n = 2$), it, therefore, cannot extend its valency beyond four [$NH_4^\oplus$, $NR_4^\oplus$]. That is the reason why nitrogen does not form NF_5 or NCl_5 . On the other hand, phosphorous and other elements have empty *d*-orbitals and can utilise all their valence electrons to exhibit covalency of five or six, e.g. PCl_5 , $[SbF_6]^\ominus$, AsF_5 , $[PF_6]^\ominus$.

2.4.3 NATURE OF BONDING

In majority of the compounds of these elements the bonds are covalent. Nitrogen and phosphorous are predominantly covalent through they may form ionic nitrides and phosphides by accepting 3 electrons. The strength of the covalent bonding decreases down the group (↓) i.e. covalent bonding strength is in the order:



2.5 CHEMICAL REACTIVITY

2.5.1 REACTIVITY TOWARDS HYDROGEN —FORMATION OF HYDRIDE

All the elements of group 15 form volatile hydrides having formula EH_3 , where E = N, P, As, Sb and Bi.

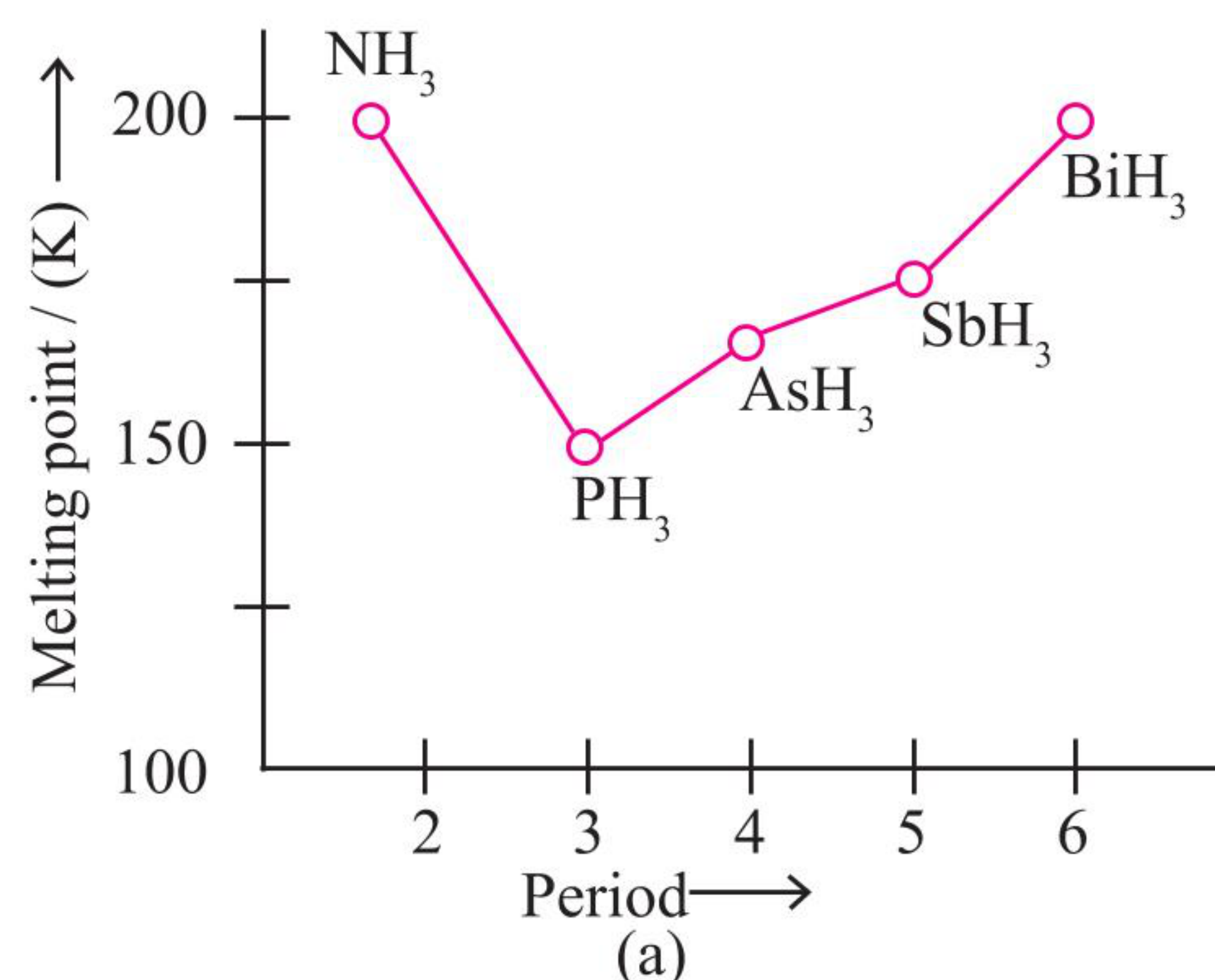
Bond angle: According to VSEPR theory, lone pair–bond pair (lp–bp) repulsion is greater than bond pair–bond pair (bp–bp) repulsion, this leads to contraction in the bond angle, i.e. bond angle is less than 109.28° (Tetrahedral angle). Consequently, all the group 15 hydrides have pyramidal shape. The bond angles are as follows:

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107.8°	93.6°	91.8°	91.3°	90°

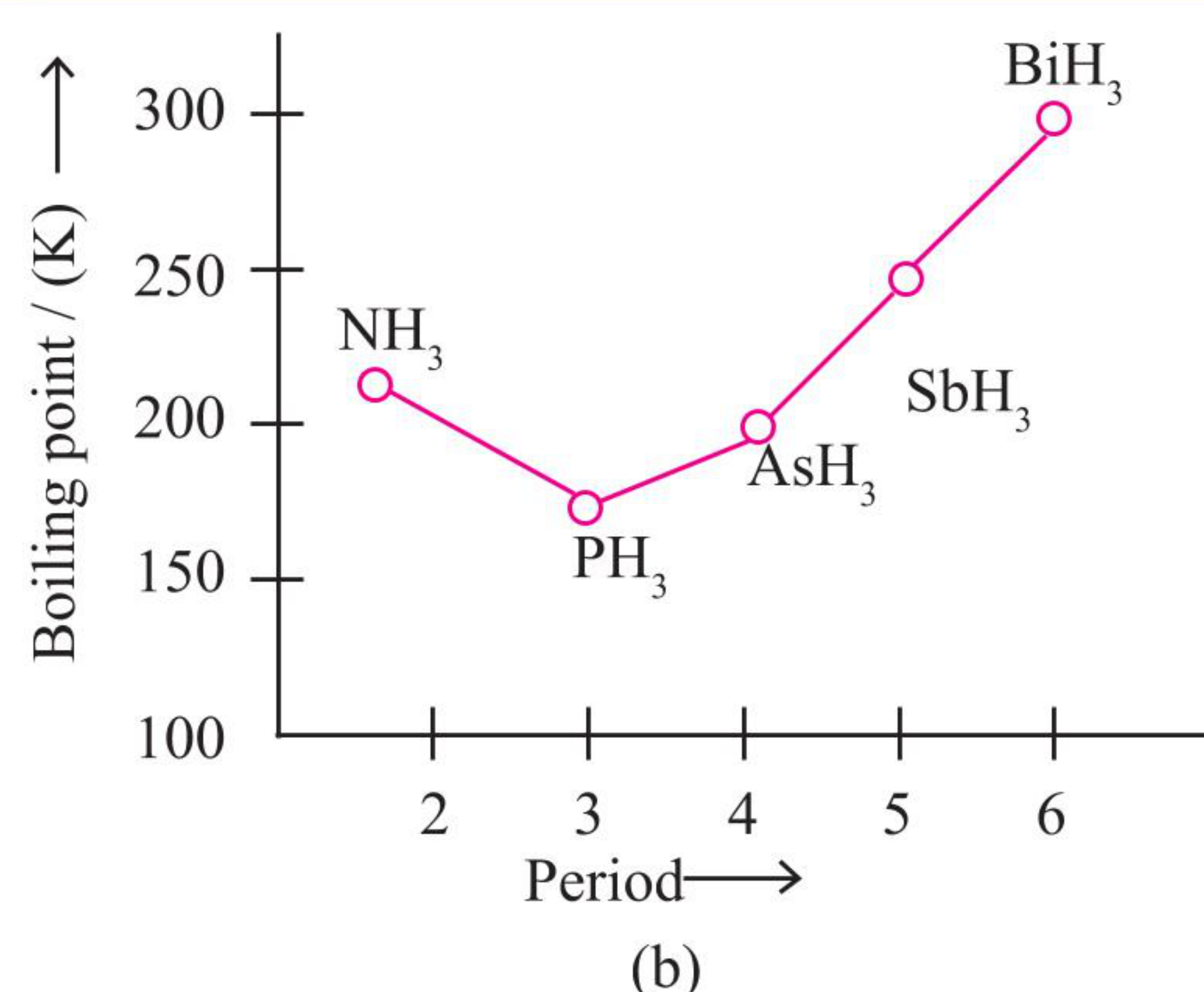
Explanation: The decrease in the bond angle can be explained on the basis of the size and electronegativity of the central atom. Due to small size and high electronegativity of N-atom, the electron density on N-atom is highest. So repulsions between the electron pairs is maximum and so is the bond angle. From N to Bi, size increases and electronegativity decreases. This results in decrease of electron density on the central atom. As a result, the repulsion between the electron pairs decreases and hence the bond angle also decreases.

2.5.2 CHARACTERISTICS OF HYDRIDES

1. Melting point and boiling point :



[Melting point: NH_3 (195.2) > BiH_3 (≈190) > SbH_3 (185) > AsH_3 (156.7) > PH_3 (139.5) K]



[Boiling point: BiH₃ (290) > SbH₃ (254.6) > NH₃ (238.5) > AsH₃ (210.6) > PH₃ (185.5) K]

Fig. 2.1 (a) and (b) Melting and boiling points of hydrides of group 15

Explanation of hydrides of group 15	
Melting point	Boiling point
The melting point of NH₃ is highest in the hydrides of group 15 due to intermolecular H-bonding. In this case increased molecular masses of BiH₃ and SbH₃ do not affect so much the melting point of NH₃. Because the increased van der Waals forces are not so strong in the solid state as they are in liquid state. OR The H-bonding in NH₃ is stronger in the solid state than in the liquid or gaseous state.	The boiling point of NH₃ is slightly lower than those of BiH₃ and SbH₃ due to their high molecular mass as compared to that of NH₃. The increased molecular masses of BiH₃ and SbH₃ increases the van der Waals forces of attraction in liquid state. OR The H-bonding in NH₃ is weaker in the liquid or gaseous state than in solid state.

2. **Thermal stability:** The thermal stability of hydrides of the elements of group 15 decreases gradually from NH₃ to BiH₃. SbH₃ and BiH₃ are thermally unstable whereas BiH₃ has been obtained in traces only.

Down the group (↓) as the bond length (internuclear) distance between hydrogen and group 15 element increases, the bond strength E–H decreases and consequently thermal stability decreases.

Thermal stability: NH₃ > PH₃ > AsH₃ > SbH₃ ≥ BiH₃

3. **Reducing agent:** The reducing character of hydrides of group 15 elements increases down the group. Because of decrease in thermal stability from NH₃ to BiH₃. The tendency to give hydrogen and act as reducing agent gradually increases from NH₃ to BiH₃. The reducing character thus depends on the instability of the hydride. The greater the instability, greater is its reducing property. Except NH₃, all the hydrides are strong reducing agents. They react with metal ions (Ag⁺, Cu²⁺ to form their phosphides, arsenides and antimonides respectively.

Reducing agent : NH₃ > PH₃ > AsH₃ > SbH₃ > BiH₃

4. **Basic character:** Ammonia is the strongest base among them. Down the group, the basic character of the hydrides of the elements of group 15 decreases. PH₃ is a much weaker base than NH₃, AsH₃, SbH₃ and BiH₃ are not basic at all.

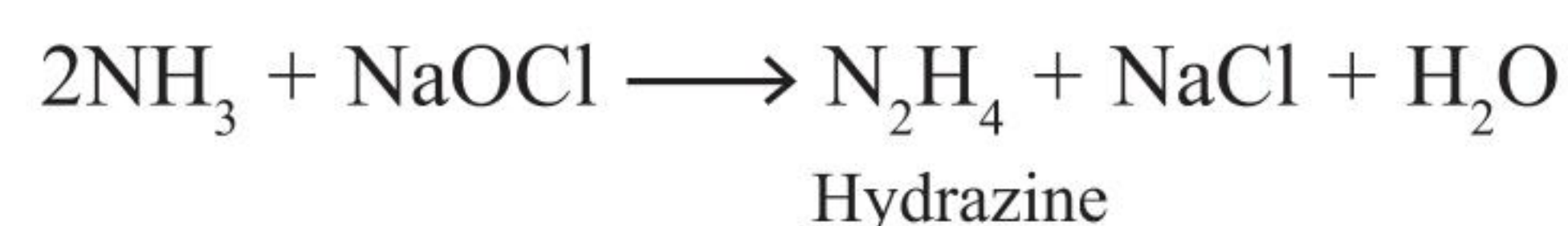
Explanation: The basic character of the hydrides of group 15 is due to the lone pair of electrons on the central atom in them (called Lewis bases).

Since the size of nitrogen atom is small, the lone pair of electrons is distributed over a small volume. As a result electron density on N is high and hence ammonia is strongly basic. Down the group, the size of the atoms (P, As, Bi etc.) goes on increasing and the lone pair of electrons is distributed over a large volume. As a result electron density decreases and, therefore, the basic strength of their respective hydrides keeps on decreasing.

5. **Solubility:** Because of tendency towards hydrogen bonding with water molecules, ammonia is soluble in water while PH₃ and other hydrides are insoluble in water.

Nitrogen and phosphorus form two other important hydrides, i.e. hydrazine (N₂H₄) and diphosphine (P₂H₄)

Hydrazine: It is prepared by the oxidation of ammonia with NaOCl (sodium hypochlorite)



Hydrazine is a strong reducing agent. Hydrazine and its derivatives are used as rocket fuels.

2.5.3 REACTIVITY TOWARDS OXYGEN (OXIDE FORMATION)

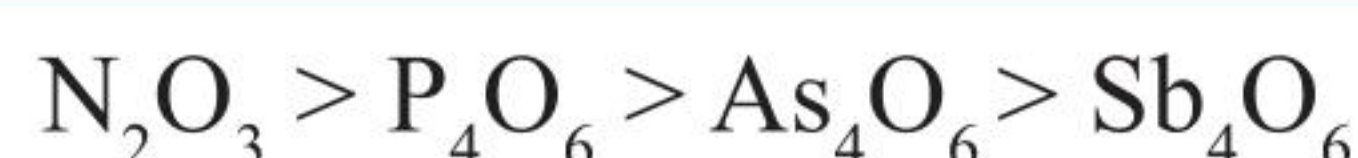
Nitrogen due to its small size has a strong tendency to form *pπ–pπ* multiple bonds between N and O atoms, while other elements of group do not. Hence nitrogen forms a number of oxides which have no P, As, Sb or Bi analogues. For example, N₂O is known but P₂O is not known.

2.5.4 PROPERTIES OF OXIDES

- Oxides of non-metals are acidic, those of metalloids are amphoteric while those of metals are basic.
- Greater the electronegativity of the element, more acidic is the oxide.
- Among the oxides of the same element, higher the oxidation state of the element, more is its acidic strength.

The oxides of the type E₂O₃ of N and P are purely acidic that of As, and Sb amphoteric and those of Bi are predominantly basic.

- Acidic strength of oxides of nitrogen increases in the order: N₂O < NO < N₂O₃ < N₂O₄ < N₂O₅ < N₂O and NO are, however, neutral.
- Acidic strength of trioxides follows the order.



In fact, As_4O_6 and Sb_4O_6 are amphoteric while Bi_2O_3 is basic in nature.

c. Acidic strength of pentoxides follows the order:



d. Due to their large size, P, As, Sb and Bi are reluctant to form $p\pi-p\pi$ multiple bond and their oxides as tetramers, X_4O_6 , X_4O_8 and X_4O_{10} . Preparation and properties of oxides of phosphorous are given in the following table and their structures are given below.

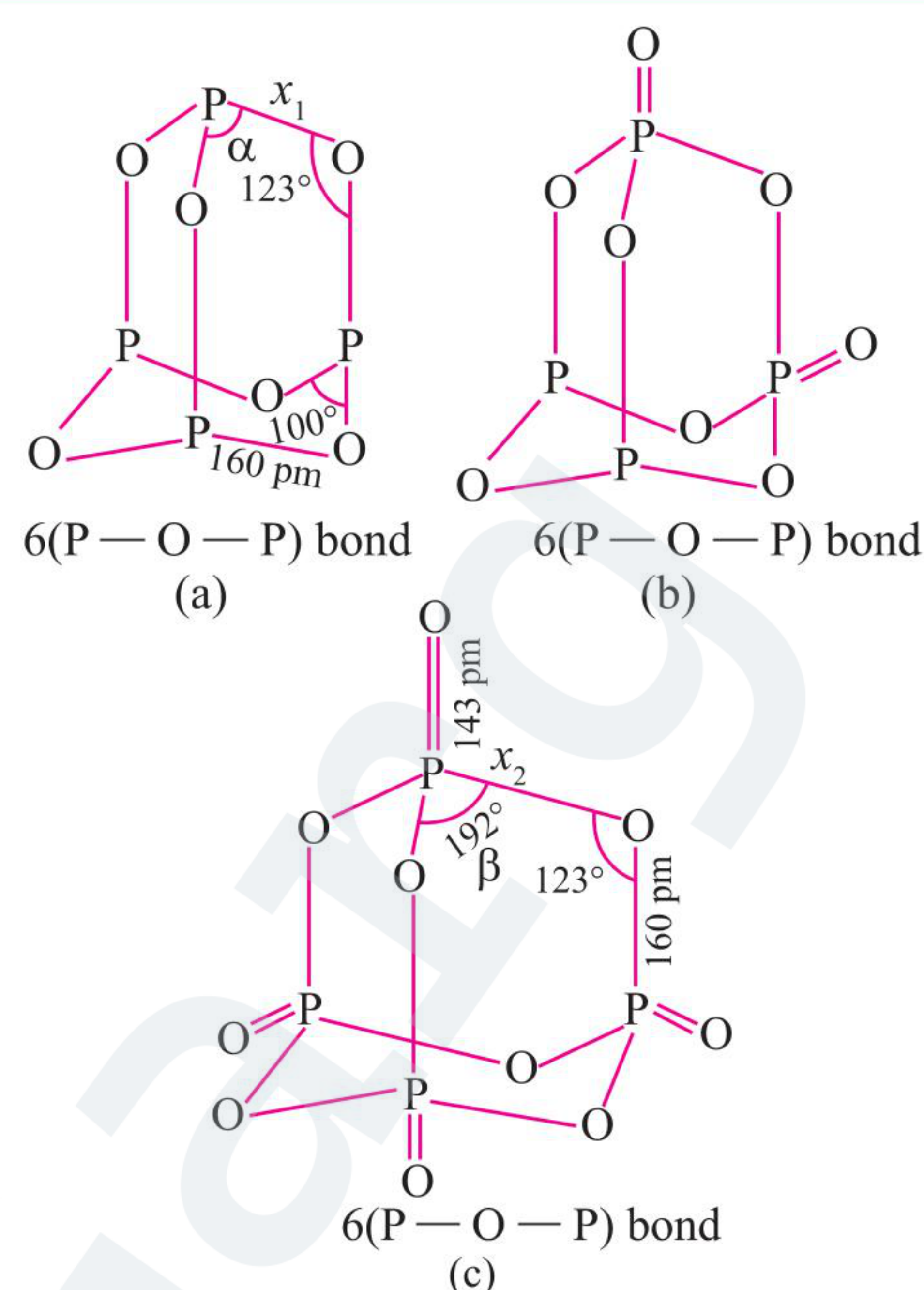
e. Trioxide of As and Sb are prepared by heating the elements in limited supply of oxygen.



Bi_2O_3 dissolves in acids to give salts



Among group 15 elements, Bi alone forms a stable nitrate, sulphate or carbonate and thus behaves like a metal. Structures of P_4O_6 , P_4O_8 and P_4O_{10} are given in Fig. 2.2.



Note : According to Bent's rule $x_1 > x_2$ and $\alpha < \beta$.

Fig. 2.2 Structure of (a) Phosphorous trioxide (P_4O_6), (b) Phosphorous tetroxide (P_4O_8) and (c) Phosphorous pentoxide (P_4O_{10})

Table 2.2 Preparation and properties of oxides of phosphorous

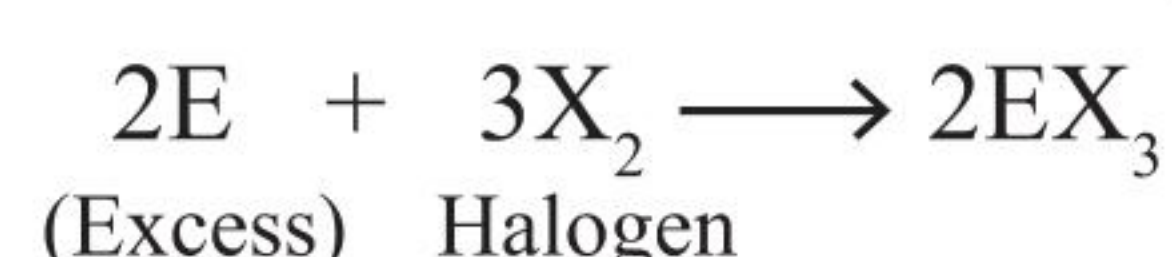
Oxides	Oxidation	Preparation	Oxides of arsenic
Phosphorous, P_4O_6	+3	Burning white P_4 in limited supply of air $\text{P}_4 + 3\text{O}_2 \rightarrow \text{P}_4\text{O}_6$	- White waxy solid, garlic smell - Soluble in ether, benzene, CS_2, CHCl_3 - With cold water phosphorous acid is formed $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_3$ - With hot water, $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{PO}_4 + \text{PH}_3$
Phosphorous tetraoxides, P_4O_8	+4	Heating P_4O_6 at 210°C in absence of air $4\text{P}_4\text{O}_6 \xrightarrow{210^\circ\text{C}} 3\text{P}_4\text{O}_8 + \text{P}_4 \text{ (Red)}$	On hydrolysis gives phosphorous acid and phosphoric acid $\text{P}_4\text{O}_8 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3 + 2\text{H}_3\text{PO}_4$
Phosphorous pentoxide, P_4O_{10}	+5	Heating white P_4 in excess of air $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$	$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$ Phosphoric acid - Acts as an excellent dehydrating agent $2\text{HClO}_4 + \text{P}_4\text{O}_{10} \rightarrow \text{Cl}_2\text{O}_7 + \text{P}_4\text{O}_{10} \cdot \text{H}_2\text{O}$

2.5.5 REACTIVITY TOWARDS HALOGENS (HALIDE FORMATION)

Group 15 elements react to form two series of halides: EX_3 and EX_5 .

2.5.5.1 Trihalides, EX_3

1. **Preparation:** The elements directly combine with halogen to form trihalides, when the group 15 element is in excess.



2. **Structures:** All the trihalides have pyramidal structure. In all the trihalides, the central halogen atom is sp^3 hybridised with 1 lp

Three of the four sp^3 hybrid orbitals overlap with np orbital of the halogen atom to form σ bond. The fourth sp^3 orbital

contains lone pair of electrons. According to VSEPR theory, since the lone pair-bond pair (lp-bp) repulsion is greater than bond pair-bond pair (bp-bp) repulsion, contraction in the bond angle occurs, hence bond angle in all the trihalides is less than 109.4° and they have pyramidal shape.

The bond angle of the trihalides of an element increases with the decrease in electronegativity of the halogen atom and increase in the size of the halogen atom.



With the decrease in the electronegativity of the halogen atom, bond pairs remain more close to the central atom and hence bp-bp repulsion increases and bond angle increases.

3. Properties:

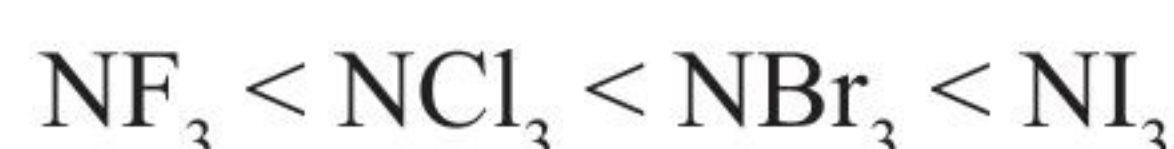
- a. All the trihalides are predominantly covalent with the ionic character increasing down the group. Thus, BiF_3 is predominantly ionic while other halides of Bi, i.e. BiCl_3 , BiBr_3 , etc. and SbF_3 are partly covalent and partly ionic.
- b. Of all the trihalides, trihalides of N, i.e. NCl_3 , NBr_3 and NI_3 are least stable. However, NF_3 is stable. NCl_3 is explosive, while NBr_3 and NI_3 are known only as their unstable ammoniates i.e. $\text{NBr}_3 \cdot \text{NH}_3$ and $\text{NH}_3 \cdot \text{NI}_3$. $\text{NI}_3 \cdot \text{NH}_3$ is stable only in moist state. In dry state it explodes with noise when struck liberating vapours of I_2 . Thus it is a mild and harmless explosive.
- $$8 \text{NI}_3 \cdot \text{NH}_3 \longrightarrow 5\text{N}_2 + 9\text{I}_2 + 6\text{NH}_4\text{I}$$

The instability of NCl_3 , NBr_3 and NI_3 is due to weakness of N–X bond due to large difference in size of N and X atoms. In NF_3 , as the difference in size of N (75 pm) and F (172 pm) is small N–F bond is quite strong. Consequently, NF_3 does not undergo hydrolysis with water, dilute acids or alkalis.

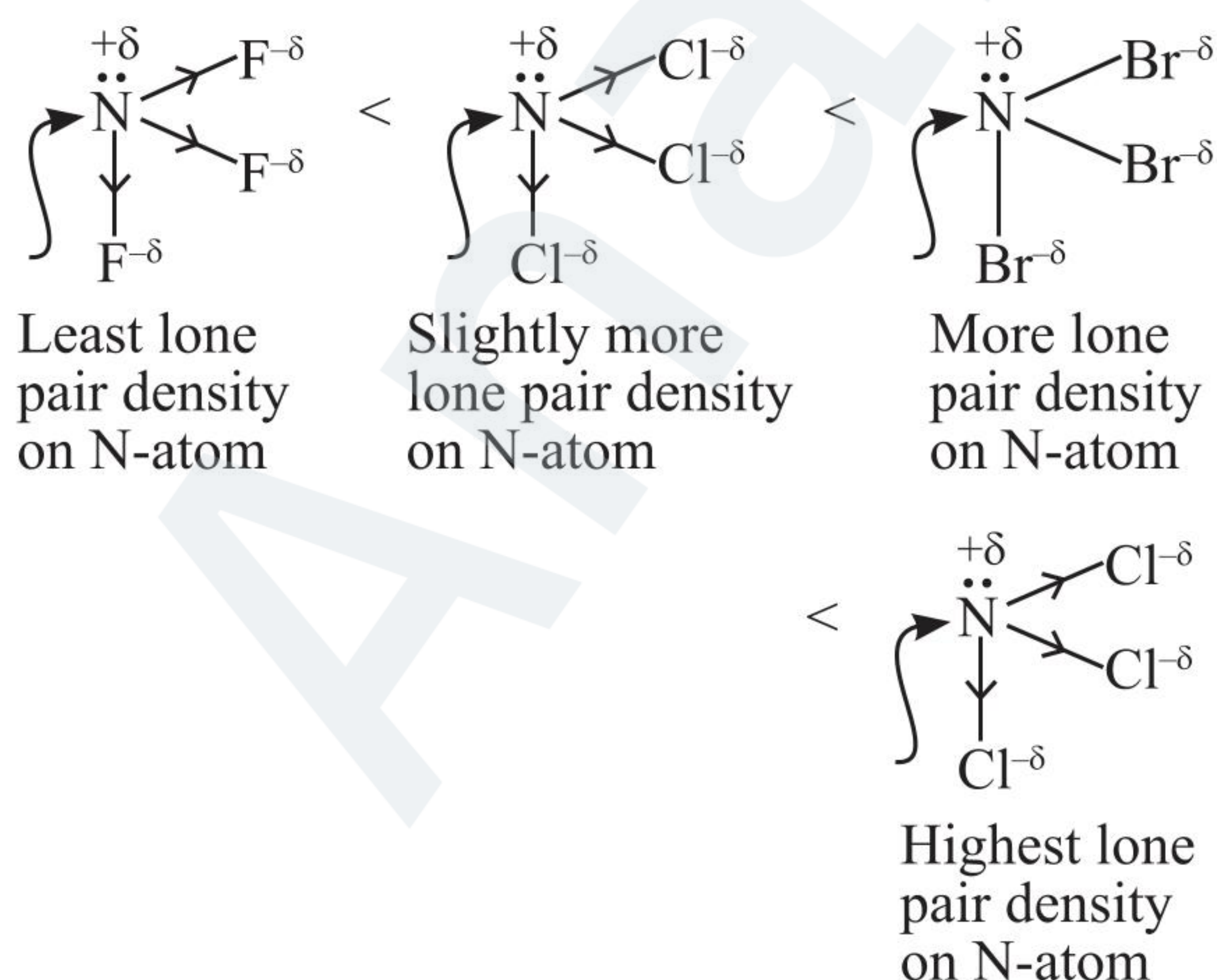
- c. **Lewis base strength of NX_3 :** Due to the presence of lone pair of electrons on N-atom and absence of d -orbitals, N-atom donates its lone pair of electrons and thus behave as Lewis bases. NF_3 behaves differently from the others. It is unreactive like CF_4 and does not hydrolyse with H_2O , dilute acids or alkalis, but reacts if sparkled with water vapour.



Lewis base strength decreases from NF_3 to NI_3 , i.e.

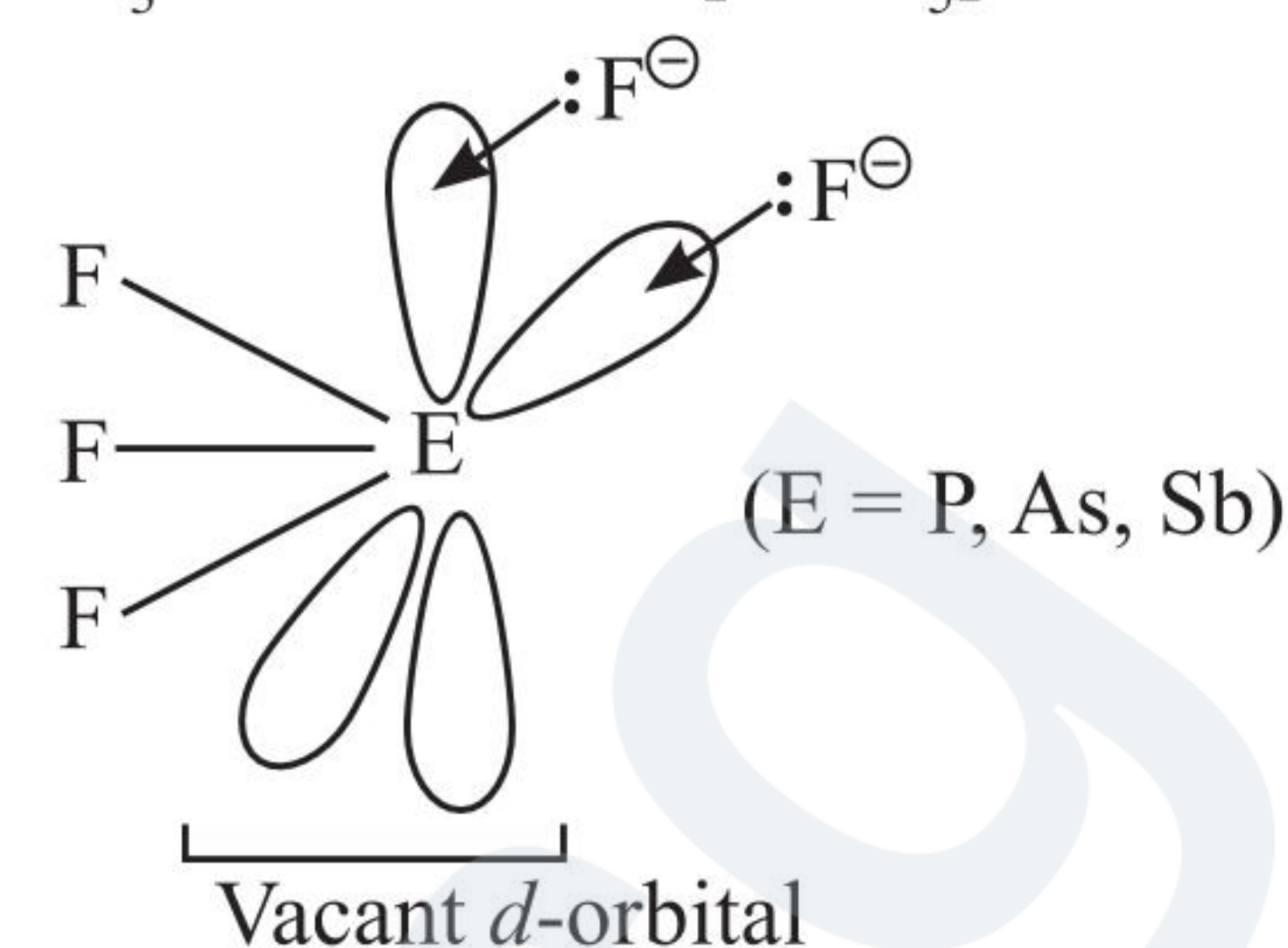
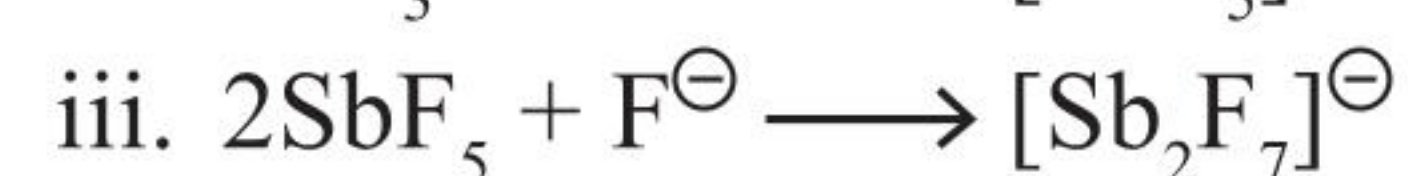
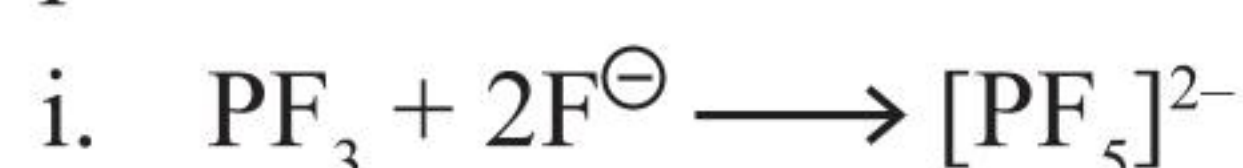


With the increase in electronegativity of halogen atom, the bond pair of N–X shifts more and more towards X-atom, hence availability of lone pair on N-atom for donation decreases and Lewis base strength decreases from NF_3 to NI_3 (EN order: $\text{F} > \text{Cl} > \text{Br} > \text{I}$).



- d. **Lewis acid strength of trihalides of P, As and Sb:**

The trihalides of P, As, Sb (especially the fluorides and chlorides) due to the presence of d -orbitals, accept lone pair of electrons and thus behaves as Lewis acids, e.g.,

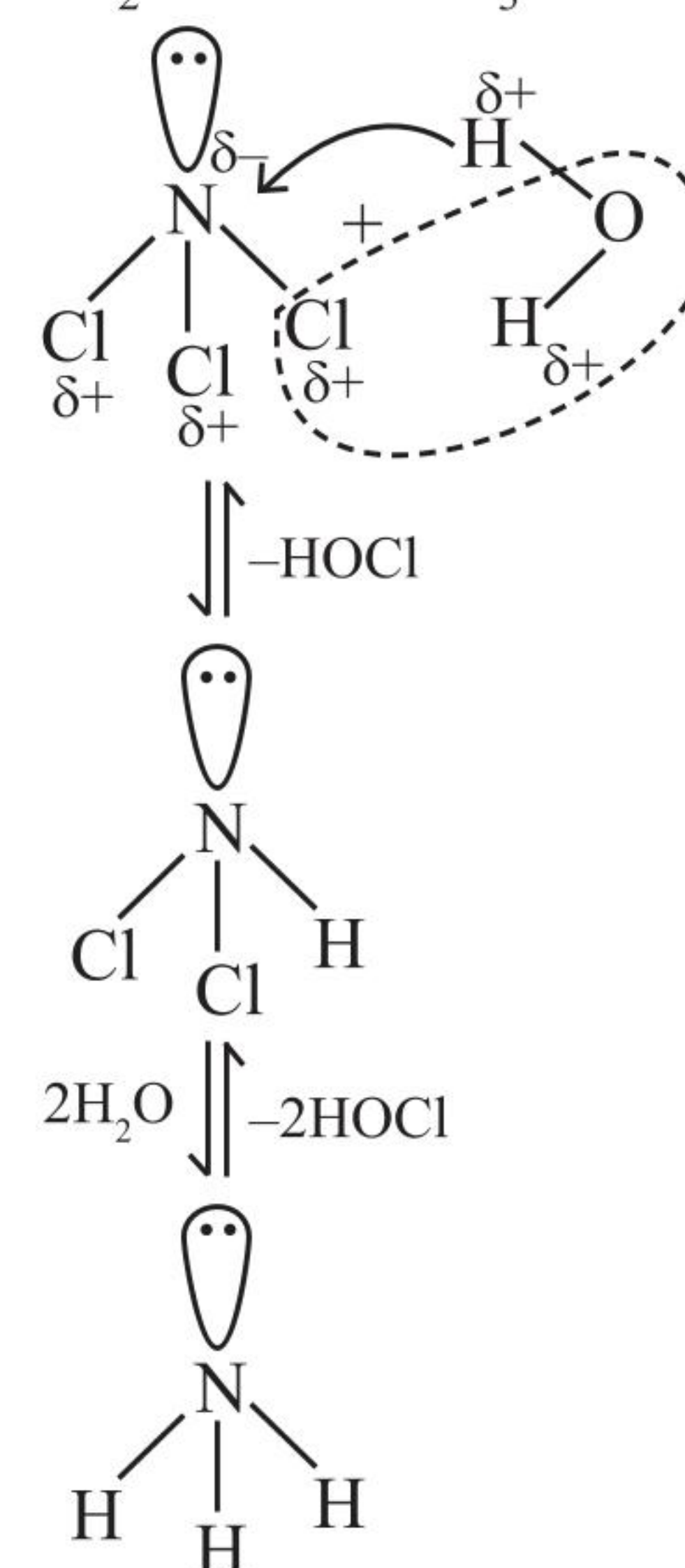
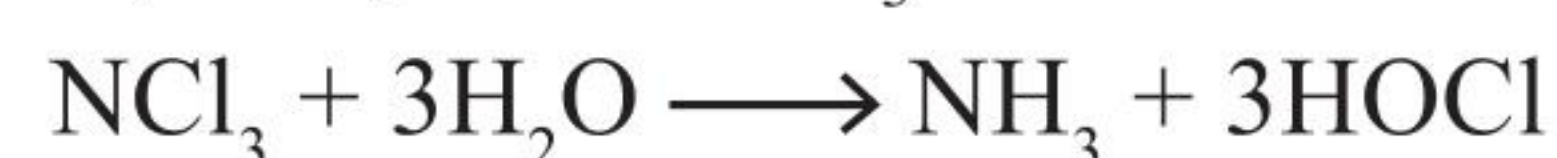


Note: PF_3 can act as donor molecules using their lone pair to form a coordinate bond. It is very similar to CO as a ligand. PF_3 is less reactive towards water and is more easily handled than other halides.

- e. **Hydrolysis:** Trihalides readily undergo hydrolysis but the product of hydrolysis depends on the nature of the bond and on the element.

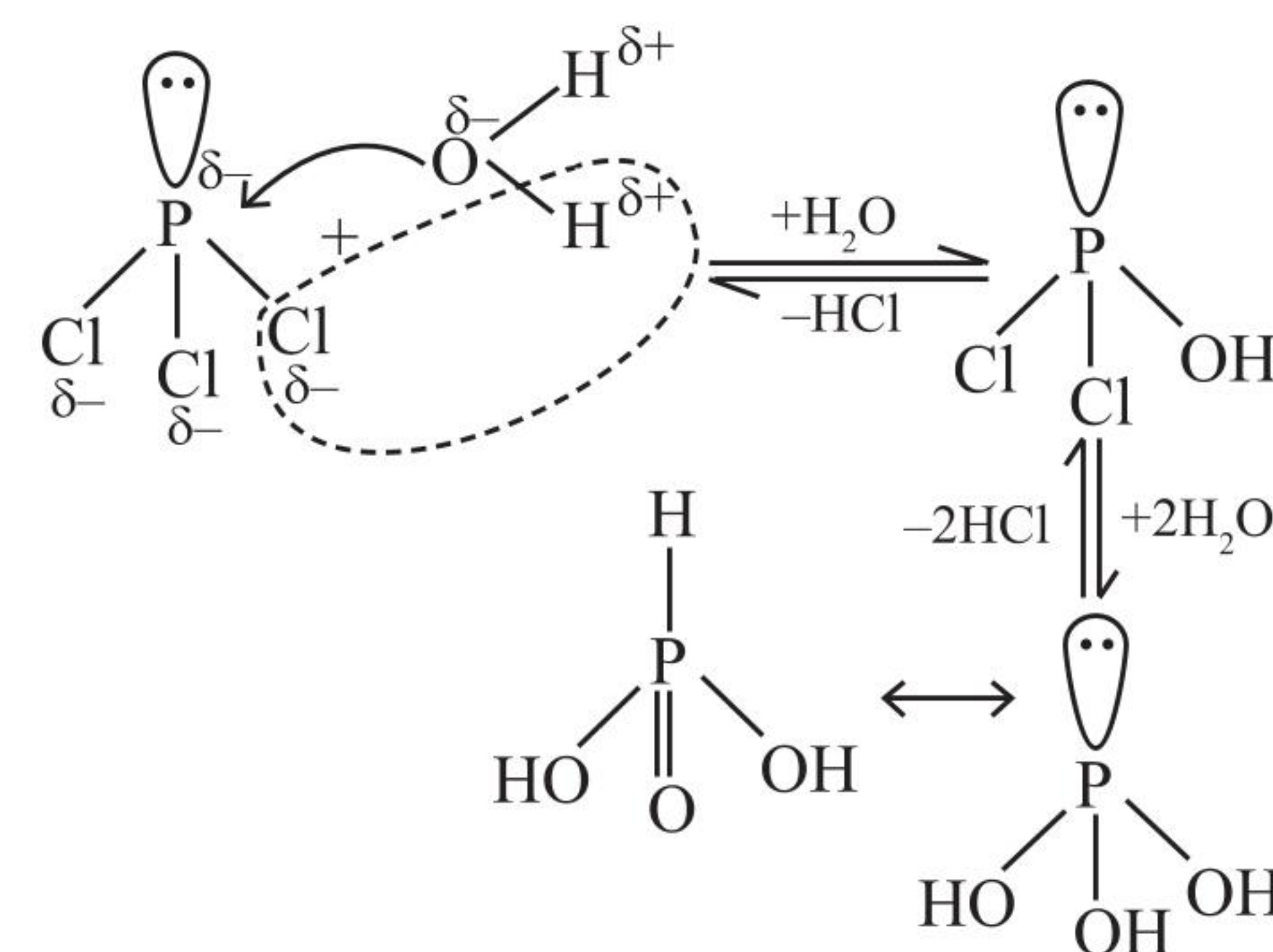
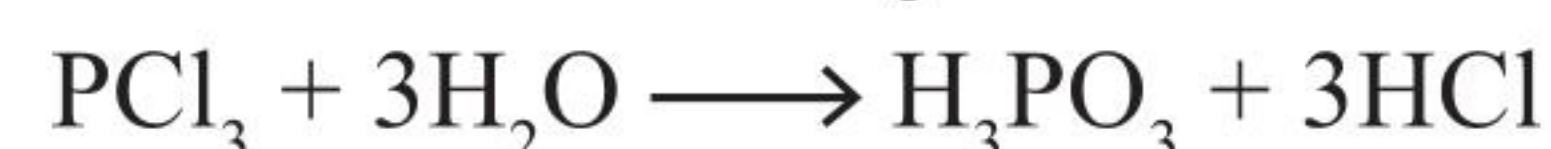
- i. NF_3 does not undergo hydrolysis, due to high N–F bond strength.

- ii. Hydrolysis of NCl_3 :



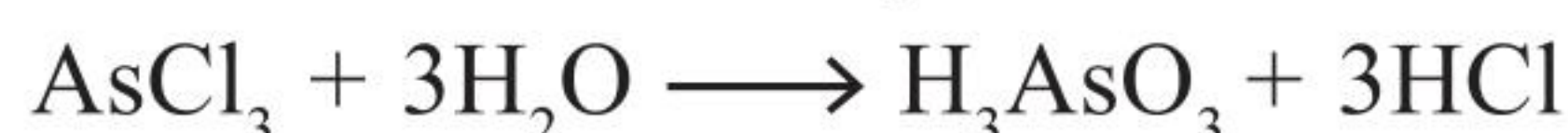
In NCl_3 , N is more electronegative than Cl, hence N interacts with the positive part of H_2O molecule and NH_3 molecule is formed, resulting in the elimination of hypochlorous acid (HOCl)

- iii. **Hydrolysis of PCl_3 :**



On the other hand in PCl_3 , P is less electronegative than Cl and P has vacant d -orbital, hence P interacts with negative part of H_2O molecule resulting in the formation of P—OH bond and elimination of HCl molecule. Consequently H_3PO_3 is formed on hydrolysis of PCl_3 .

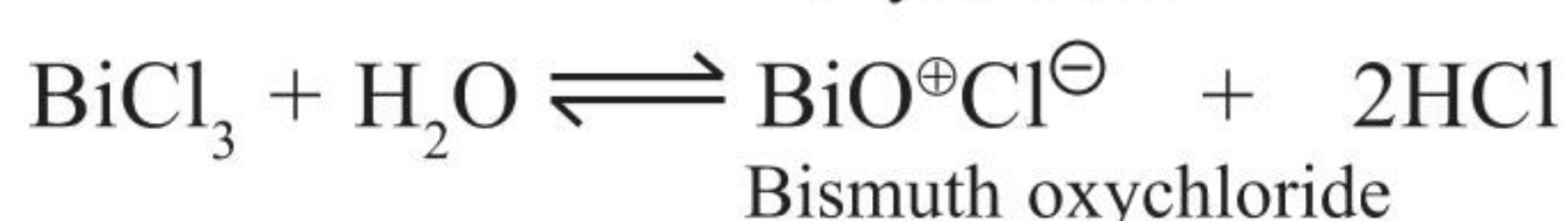
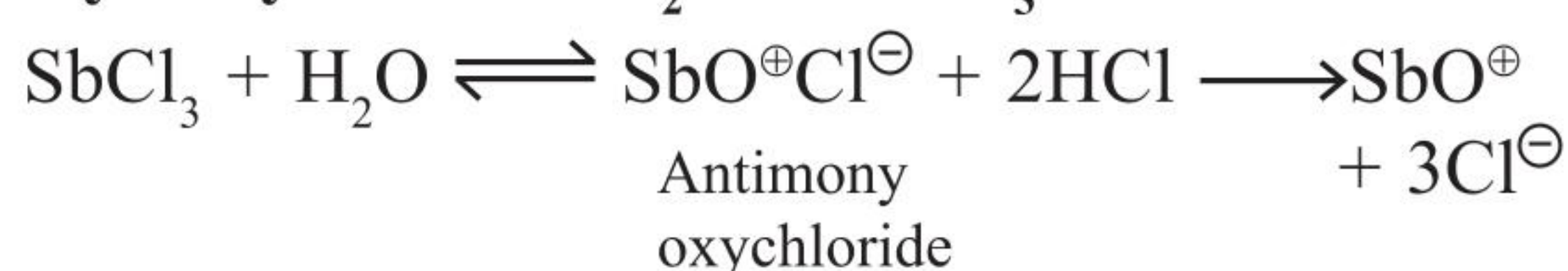
iv. Hydrolysis of AsCl_3 :



Trichlorides of As on hydrolysis gives arsenic acid (H_3AsO_3) and HCl.

Trichlorides of Bi and Sb are only partly and reversibly hydrolysed to give HCl and oxychloride of the corresponding metal, i.e.

v. Hydrolysis of SbCl_3 and SnCl_3 :



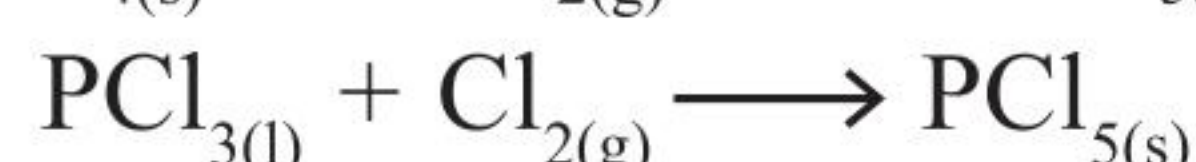
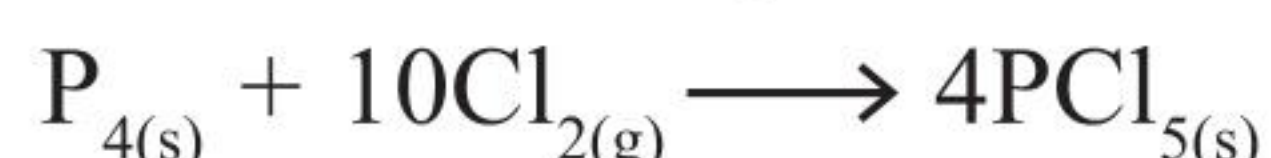
According to **Le Chatelier principle**, the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left.

2.5.5.2 Pentahalides, EX_5

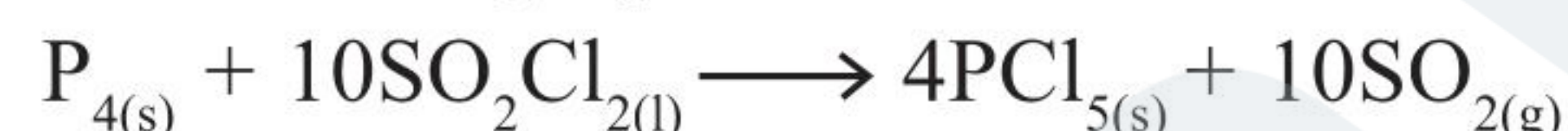
1. Nitrogen does not form pentahalides, NX_5 as N due to absence of d -orbitals in its valence shell cannot expand its coordination number beyond 4.

Phosphorous pentachloride, PCl_5 :

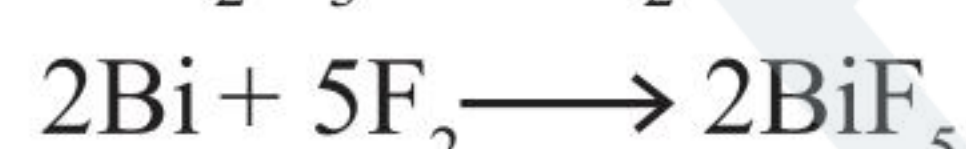
- (1) Phosphorous pentachloride is prepared by the reaction of white phosphorous with excess of dry chlorine or by the action of dry chlorine on phosphorous trichloride.



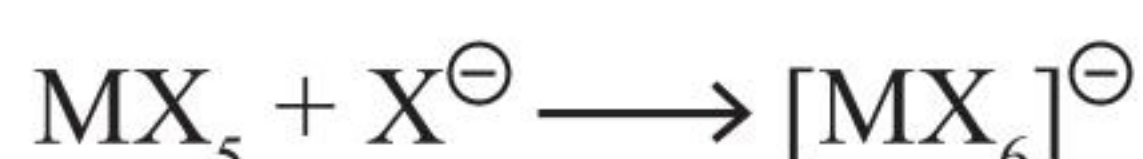
- b. It can also be prepared by the action of sulphuryl chloride (SO_2Cl_2) on white phosphorous.



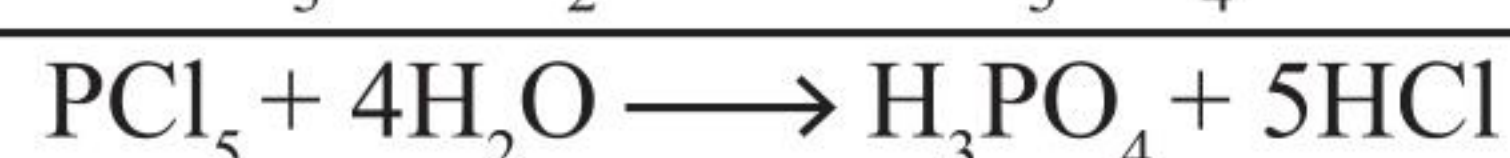
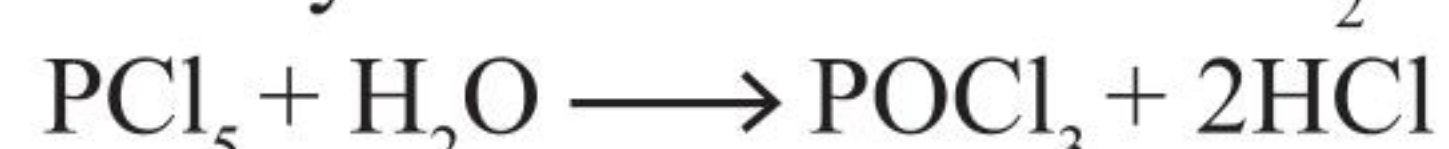
- c. AsCl_5 is highly reactive and unstable and has only a temporary existence. BiF_5 is highly reactive, and explodes with water, forming O_3 and F_2O . It oxidises UF_4 to UF_6 and BrF_3 to BrF_5 , and fluorinates hydrocarbons. The pentahalides are prepared as follows:



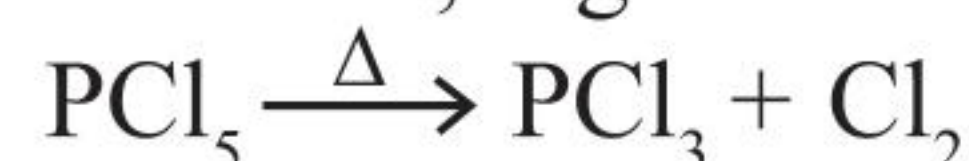
2. All the pentahalides behave as **Lewis acids** due to presence of vacant d -orbital on the central atom.



3. PF_5 does not undergo hydrolysis due to high stability of P—F bond as compared to P—O bond. However, all other pentahalides of P, undergo hydrolysis to give POCl_3 initially and with excess of H_2O gives H_3PO_4 .



4. Pentahalides are thermally less stable than the corresponding trihalides, e.g. thermal stability of PCl_5 is less than PCl_3 .



That is why PCl_5 behaves as a good chlorinating agent.

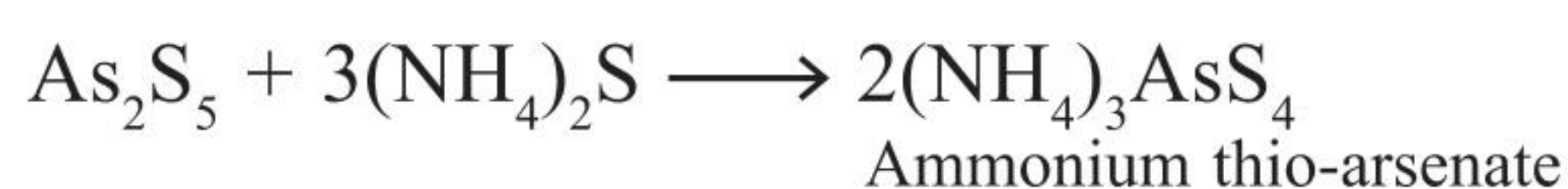
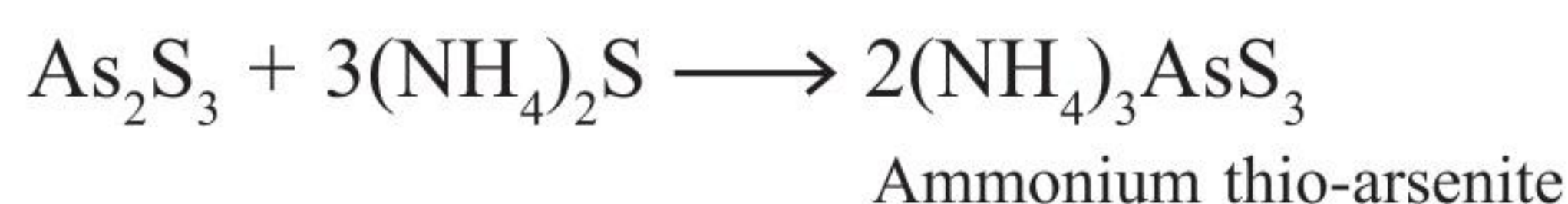
5. **Structure:** In gaseous state, PX_5 are covalent and have trigonal bipyramidal structure as P is sp^3d hybridised. Whereas in solid state, pentahalides of phosphorous are ionic and exist as given below.

PX_5	Gas	Solid
Phosphorous pentachloride	PCl_5	$[\text{PCl}_4]^\oplus [\text{PCl}_6]^\ominus$
Phosphorous pentabromide	PBr_5	$[\text{PBr}_4]^\oplus [\text{Br}]^\ominus$
Phosphorous pentaiodide	PI_5	$[\text{PI}_4]^\oplus [\text{I}]^\ominus$

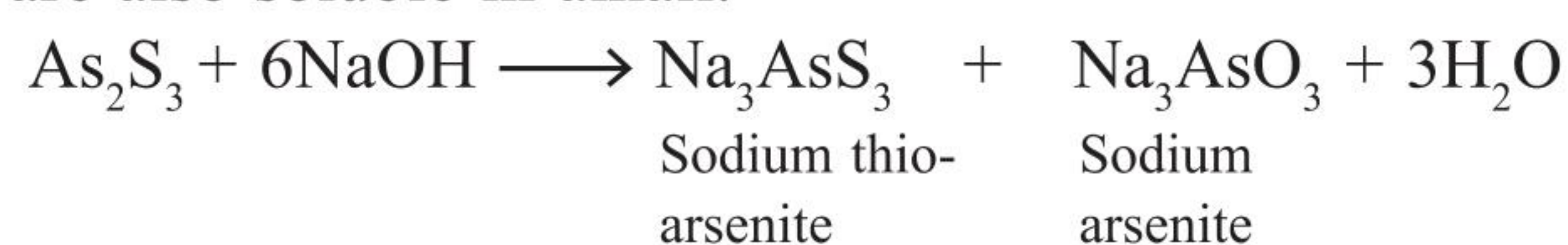
2.5.6 REACTIVITY TOWARDS METALS

1. All the group 15 elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as Ca_3N_2 (calcium nitride), Ca_3P_2 (calcium phosphide) Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

2. **Sulphide formation:** Except nitrogen all other group 15 elements form sulphides. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide or ammonium sulphide and form thio-compounds.



Antimony sulphides form similar compounds. The sulphides are also soluble in alkali.



The stability of sulphides increases with increase in atomic number of the element.

2.6 ANOMALOUS BEHAVIOUR OF NITROGEN

Nitrogen shows anomalous behaviour and differs from rest of the members of its family due to:

- i. Small size
- ii. High electronegativity
- iii. High ionisation enthalpy
- iv. Non-availability of d -orbitals in its valence shell.

Some important properties in which nitrogen differs from other members of group 15 are as follows:

1. Nitrogen exists as a diatomic (N_2) gas, while others exist as tetrahedral tetraatomic solid molecules (P_4 , As_4 and Sb_4).
2. Nitrogen shows less catenating ability than phosphorous.

3. Nitrogen is inert and unreactive in its elemental state, whereas others are highly reactive.
4. Nitrogen due to absence of d -orbitals in its valence shell shows a maximum covalency of four, i.e. nitrogen cannot expand its covalency beyond four, e.g. NH_4^+ . Other group 15 elements due to presence of vacant d -orbitals in their valence shell can have a coordination number 5 or 6 e.g. PF_5 , $[\text{PF}_6]^-$.
5. Nitrogen due to absence of d -orbitals in its valence shell, cannot form $d\pi-p\pi$ bonds, whereas others can. For example, $\text{R}_3\text{N}=\text{O}$ does not exist, but $\text{R}_3\text{P}=\text{O}$ exists.
6. Due to small size and high electronegativity, nitrogen forms trinegative N^{3-} ion. This tendency is less in phosphorous and absent in others.
7. Hydride of nitrogen, NH_3 is stable, while other hydrides are not stable. NH_3 is capable of forming hydrogen bonding while others do not.
8. Nitrogen forms five oxides (N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5). Whereas, phosphorous forms three dimeric oxides (P_4O_6 , P_4O_8 , P_4O_{10}). Arsenic and antimony form only two dimeric oxides (As_4O_6 , As_4O_{10} , Sb_4O_6 , Sb_4O_{10}). Bismuth forms Bi_2O_3 only.
9. Except NF_3 , the other trihalides of nitrogen, i.e. NCl_3 , NBr_3 and NI_3 are unstable. On the other hand, trihalides of other elements stable.
10. Nitrogen does not form pentahalides, whereas P, As and Sb form pentahalides.
11. Nitrogen shows a large number of oxidation states from -3 to $+5$ other group 15 elements show a limited number of oxidation states.

ILLUSTRATION 2.1

- a. Though nitrogen exhibits $+5$ oxidation state, it does not form pentahalide. Give reason.
- b. PH_3 has lower boiling point than NH_3 . Why?

- Sol.**
- a. Electronic configuration of nitrogen is $1s^2 2s^2 2p^3$. Due to absence of d -orbitals in its valence shell, nitrogen cannot expand its coordination number beyond four. That is why nitrogen does not form pentahalides.
 - b. Nitrogen is more electronegative than phosphorous and hence capable of forming hydrogen bonds. Due to association of NH_3 molecules by hydrogen bonding, ammonia has higher boiling point. On the other hand, due to absence of hydrogen bonding in PH_3 molecules are not associated and PH_3 has lower boiling point than NH_3 .

ILLUSTRATION 2.2

- a. PF_5 is known, but NF_5 is not. Why?
- b. The experimentally determined $\text{N}-\text{F}$ bond length in NF_3 is greater than the sum of single covalent radii of N and F.

- Sol.**
- a. Phosphorous has vacant d -orbital in its valence, hence P can have covalency of five and PF_5 exists. But, N due to absence of d -orbital in its valence shell cannot have covalency of five, hence NF_5 is not known.
 - b. Due to their smaller size and high electron density, experimentally determined $\text{N}-\text{F}$ bond length is high, because of repulsion of bonded pair of both N and F atoms.

ILLUSTRATION 2.3

- a. Why elemental phosphorous does not exist as P_2 like N_2 ?
- b. NCl_3 gets easily hydrolysed, while NF_3 does not. Why?

- Sol.**
- a. Nitrogen due to its small size has a tendency to form multiple bond and thus exists as diatomic molecule. Phosphorous, on the other hand, has comparatively large size, therefore, extent of overlap of $(3p-3p)$ which can result in π -bond formation is less, and phosphorous has no tendency to form multiple bond with itself. Hence phosphorous does not exist as P_2 molecule.
 - b. In NCl_3 , N is more electronegative than Cl, hence N has δ^- charge and Cl has δ^+ charge, moreover due to presence of vacant d -orbital on Cl, it accepts a pair of electron from O atom of H_2O molecule. Thus hydrolysis is possible. On the other hand, in NF_3 due to high $\text{N}-\text{F}$ bond strength, NF_3 molecule is inert and does not undergo hydrolysis.

ILLUSTRATION 2.4

- a. Can PCl_5 act as an oxidising as well as reducing agent?
- b. Phosphorous does not form phosphorous pentafluoride. Why?

- Sol.**
- a. In PCl_5 , oxidation state of P is $+5$. Phosphorous can exhibit a maximum oxidation state of $+5$. Since P cannot have oxidation state greater than $+5$. Therefore, it cannot get oxidised and thus PCl_5 cannot act as reducing agent. However, P can have lower oxidation state as compared to $+5$, and thus can get reduced and PCl_5 behave as oxidising agent.
 - b. Due to large size of iodine, phosphorous cannot accommodate five iodine atoms around it, and hence PI_5 does not exist. Moreover EN of iodine is too low to excite $3s^2$ electron to $3d$ orbitals for the formation of five bonds.

ILLUSTRATION 2.5

- a. Heavier metals of 15 group do not form $p_\pi-p_\pi$ bonds. Why?
- b. Why $\text{N}-\text{N}$ bond is weaker than single $\text{P}-\text{P}$ bond.

- Sol.**
- a. Nitrogen has unique ability to form $p_\pi-p_\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier metals of this group do not form $p_\pi-p_\pi$ bonds.

as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, Nitrogen exists as diatomic molecule with a triple bond (one *s* and two *p*) between two atoms.

Consequently, its bond enthalpy (971.4 kJ mol⁻¹) is very high. On the contrary, P, As and Sb form single bonds as P—P, As—As and Sb—Sb while Bi forms metallic bond in elemental state.

- b. It is due to high interelectronic repulsion of the non-bonding e⁻s, owing to the small bond length. As a result catenation tendency is weaker in nitrogen.

2.7 DINITROGEN (N₂)

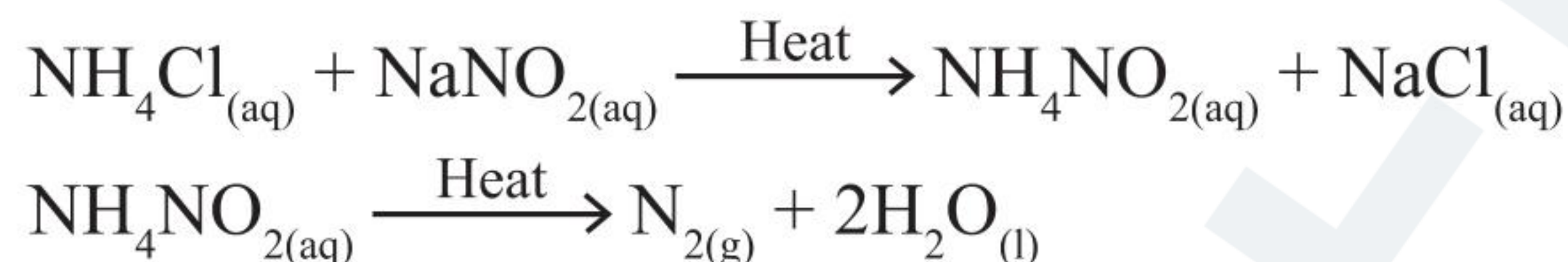
Nitrogen exists as a diatomic gas, N₂ in the elemental state, hence it is also known as dinitrogen.

Preparation:

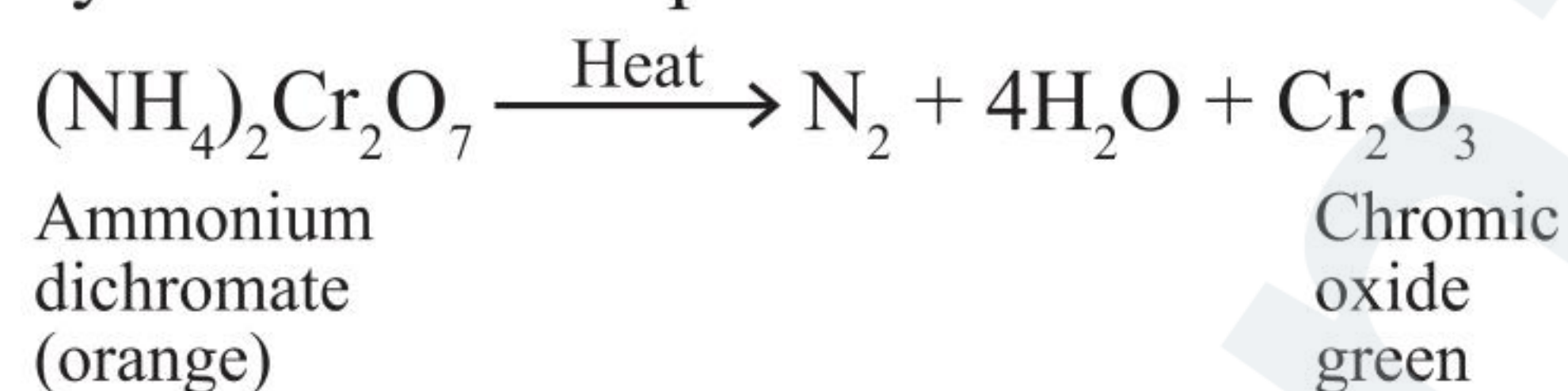
1. **Commercial method:** Dinitrogen is prepared commercially by the liquefaction and fractional distillation of air. On distillation, liquid dinitrogen having lower boiling point (77.2 K) distils out first leaving behind liquid oxygen having higher boiling point (90 K).

2. **Laboratory method:**

- a. By heating an equimolar aqueous solution of ammonium chloride (NH₄Cl) with sodium nitrite, (NaNO₂). As a result of double decomposition reaction, ammonium nitrite (NH₄NO₂) is formed first, which being unstable decomposes immediately to form dinitrogen gas.



- b. By thermal decomposition of ammonium dichromate:



- c. By thermal decomposition of sodium or barium azide: Very pure nitrogen can be obtained by this method.



Thermal decomposition of sodium azide is used to inflate the air bags used for safety devices in cars.

2.7.1 PROPERTIES

2.7.1.1 Physical Properties

- Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
- Nitrogen atom has two stable isotopes: ¹⁴N and ¹⁵N.
- It has very low solubility in water (23.2 mL/L of water at 273 K and 1 bar pressure).
- It has low freezing (63.2 K) and boiling point (77.2 K).
- It is absorbed by activated charcoal.

2.7.1.2 Chemical Properties

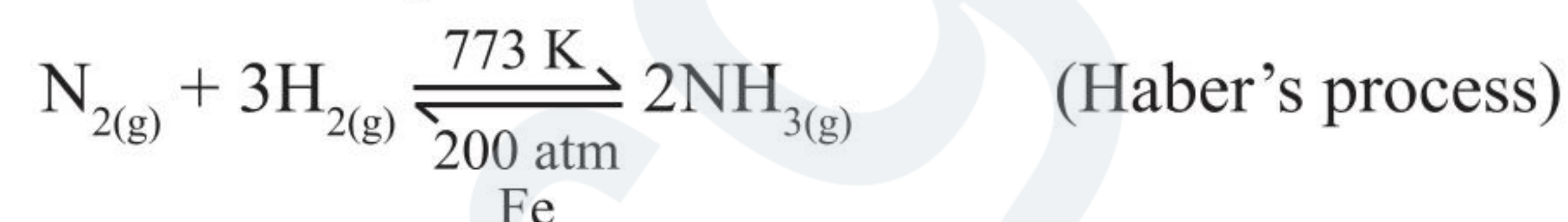
- Dinitrogen is an inert gas due to very small N≡N bond length and hence high bond dissociation enthalpy. However, reactivity increases with increase in temperature.

- Reaction with metal:** The nitrides formed with active metals are predominantly ionic.

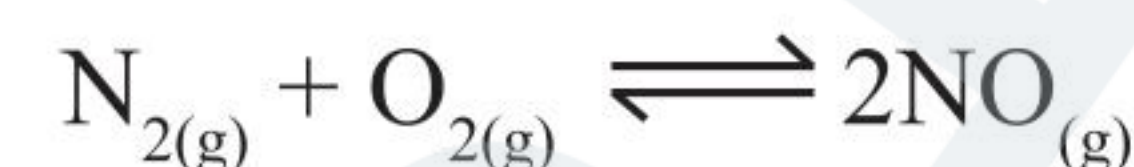


- Reaction with non-metals:** Dinitrogen reacts with non-metals to form predominantly covalent nitrides.

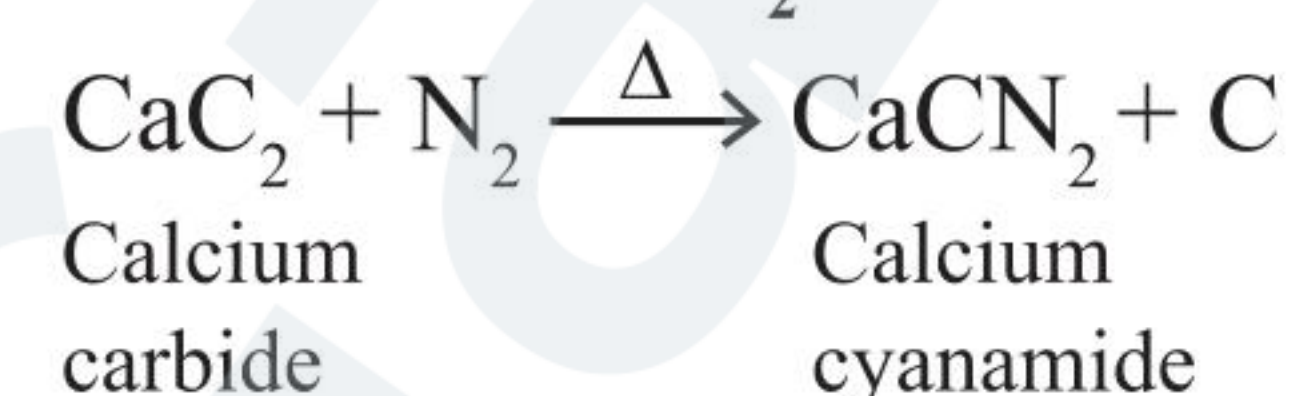
- a. With H₂, N₂ reacts at ~773 K and 200 atm in the presence of Fe as catalyst to form ammonia.



- b. With O₂, N₂ combines at a very high temperature, i.e. ~2000 K form nitric oxide, NO.



- Reaction with CaC₂:**



- Calcium cyanamide reacts with water to form NH₃, hence, it is used as a fertiliser under the name Nitrolim (CaCN₂ + C).

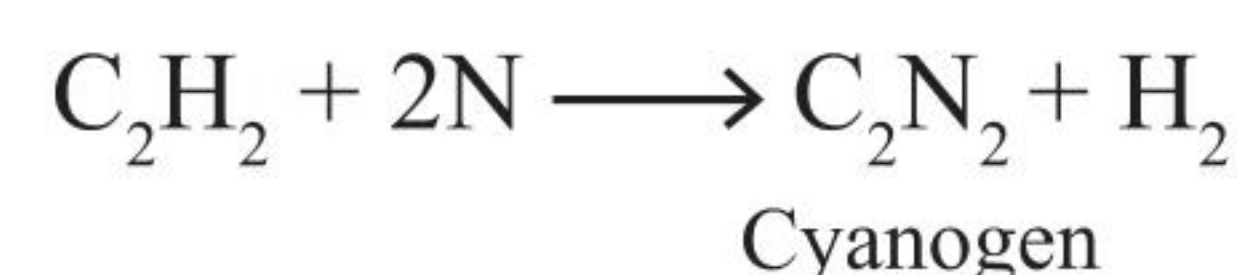


Uses:

- In the manufacture of ammonia and other industrial chemical containing nitrogen, e.g. calcium cyanamide.
- To provide an inert atmosphere in iron and steel industry. It also acts as a inert diluent (for reactive chemicals).
- Liquid nitrogen is used as a refrigerant, to preserve biological materials, food items and in cryosurgery.
- In gas filled thermometers, which are used for measuring high temperatures.
- To fill electric bulbs, hence reducing the rate of volatilisation of the tungsten filament.

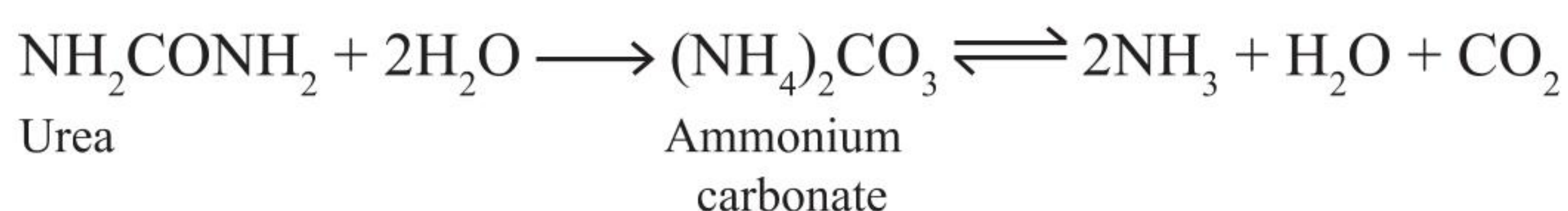
2.7.2 ACTIVE NITROGEN

Active nitrogen is made by passing an electric spark through N₂ gas at 2 mm pressure. This forms atomic nitrogen (N) and the process is associated with yellow-pink after glow. It decomposes many organic compounds.



2.8 AMMONIA (NH₃)

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter, e.g. urea



Preparation:



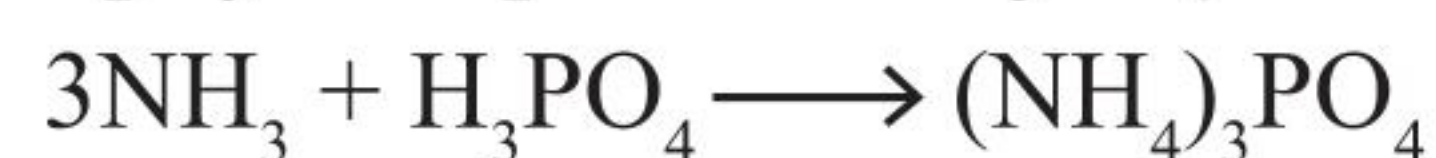
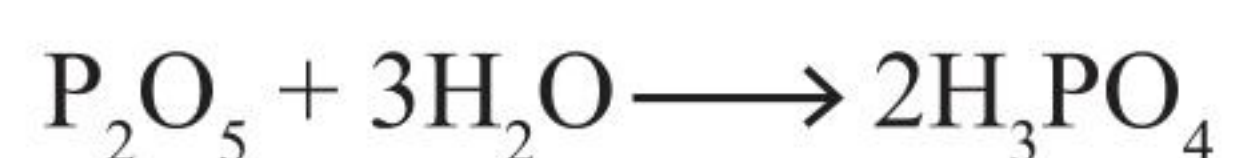
Slaked lime



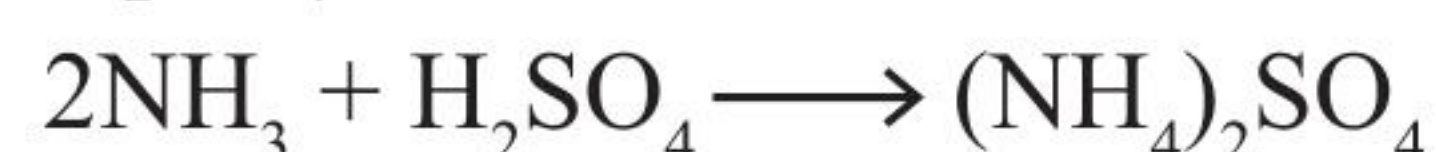
4. Ammonia cannot be dried by:

a. **Anhydrous CaCl_2 :** NH_3 forms a complex with CaCl_2 .
 $\text{CaCl}_2 + 8\text{NH}_3 \longrightarrow \text{CaCl}_2 \cdot 8\text{NH}_3$

b. **Phosphorous pentoxide:** NH_3 reacts with P_2O_5 to form ammonium phosphate.



c. **Concentrated sulphuric acid:** NH_3 reacts with conc. H_2SO_4 to form ammonium sulphate.



5. Manufacture of ammonia: On commercial scale, ammonia is manufactured by **Haber's process**.



This reaction is reversible, exothermic and occurs with decrease in volume. In accordance with **Le Chatelier's principle**, the favourable conditions for the manufacture of ammonia are:

a. **Low temperature:** As the forward reaction is exothermic, low temperature will favour the formation of ammonia. The optimum temperature for the reaction has been found to be $\sim 700 \text{ K}$.

b. **High pressure:** As the forward reaction occurs with decrease in volume, high pressure will favour the formation of ammonia. The optimum pressure for the reaction is about $200 \times 10^5 \text{ Pa}$ or 200 atm .

c. **Catalyst:** Rate of reaction at 700 K and 200 atm pressure is increased by the use of catalyst such as iron oxide with small amount of K_2O and Al_2O_3 . Sometimes, molybdenum is used as a promoter (promoter increases the efficiency of the catalyst). Flow chart for the production of ammonia is given in Fig. 2.3.

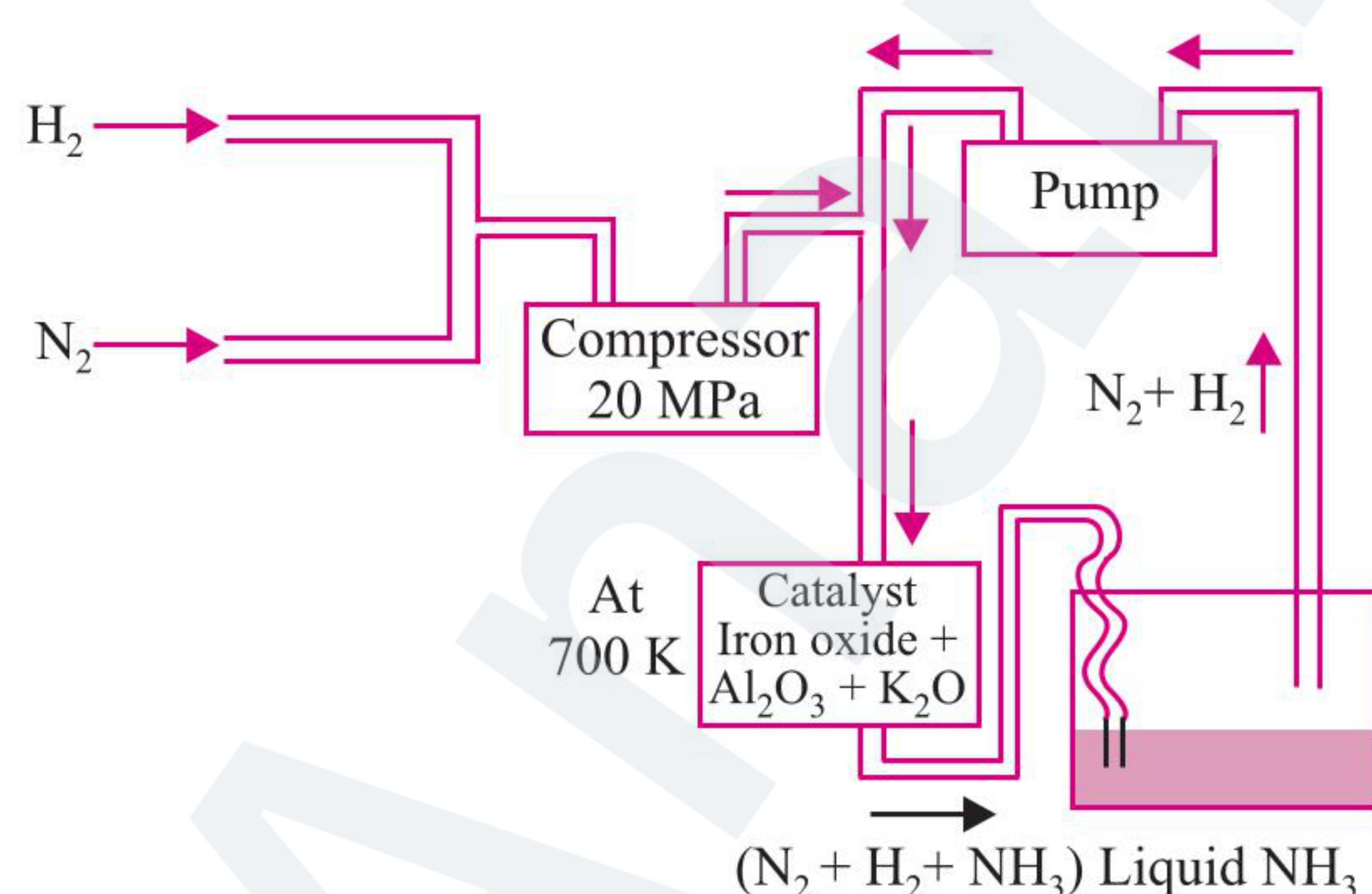


Fig. 2.3 Flow chart for the manufacture of NH_3 by Haber process

2.8.1 PROPERTIES

2.8.1.1 Physical Properties

1. Ammonia is a colourless gas with a characteristic pungent odour. It brings tears into the eyes.
2. It is lighter than air (density = 0.68 g cm^{-3}).
3. It is highly soluble in water. One volume of water dissolves 1300 volumes of ammonia at 0°C at 1 atm pressure. The high solubility in water is due to hydrogen bonding. The

solubility of ammonia increases with increase of pressure and decreases with increase of temperature.

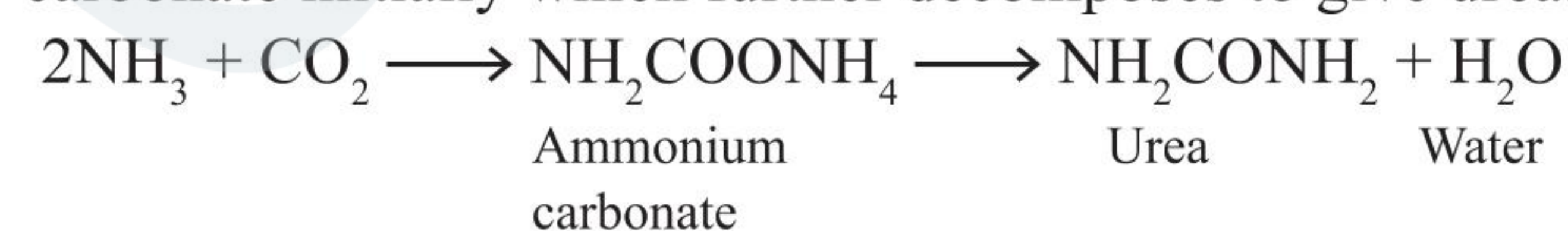
4. It can be easily liquefied at room temperature by the application of pressure. Liquid ammonia is colourless and boils at 239.7 K and freezes at 198.4 K . In the solid and liquid state, it is associated through hydrogen bonds as in the case of water that accounts for its higher boiling and melting points than expected in comparison to other group 15 hydrides, on the basis of its molecular mass.
5. On vapourisation, liquid ammonia causes intense cooling.

2.8.1.2 Chemical Properties

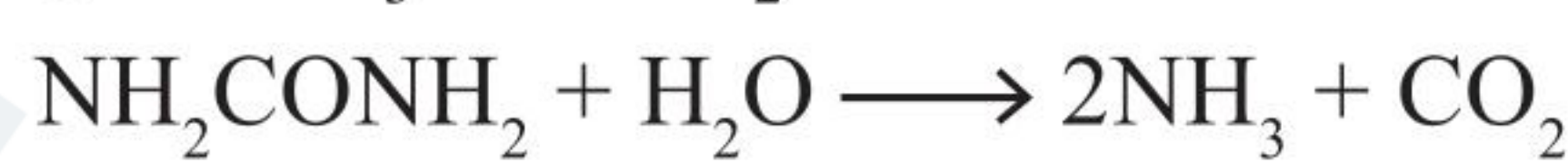
1. **Reaction with metals:** Ammonia reacts with Na or K metal to form corresponding amides and hydrogen is liberated.



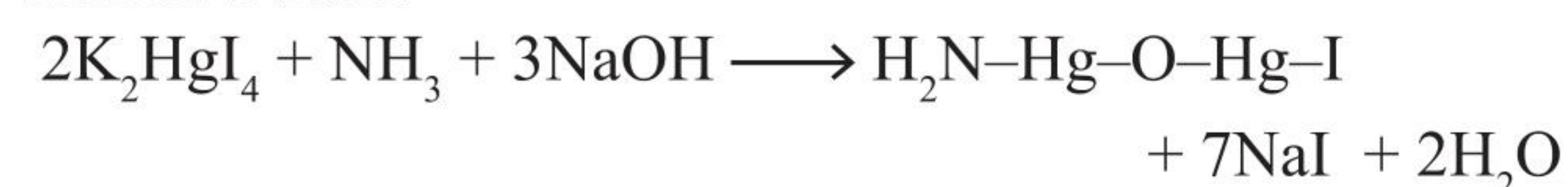
2. **Reaction with CO_2 :** Liquid NH_3 reacts with gaseous CO_2 at $453\text{--}473 \text{ K}$ and 220 atmospheres to form ammonium carbonate initially which further decomposes to give urea.



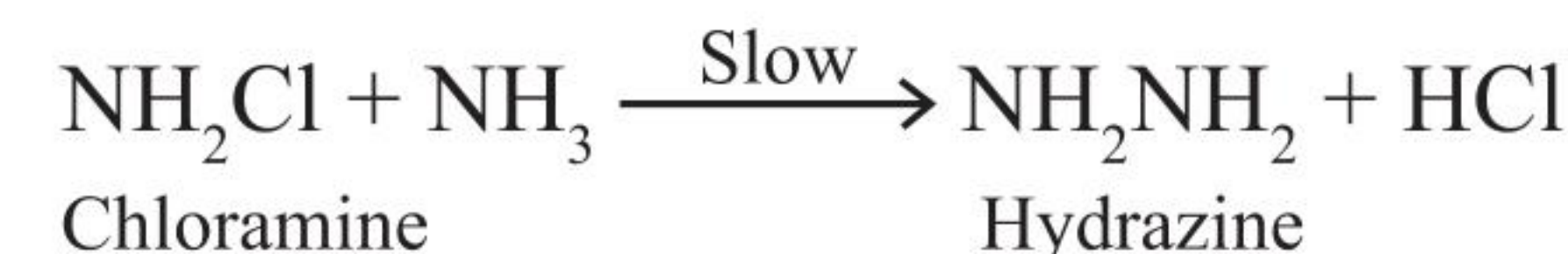
Urea is used as fertiliser as it decomposes slowly in soil to give NH_3 and CO_2 .



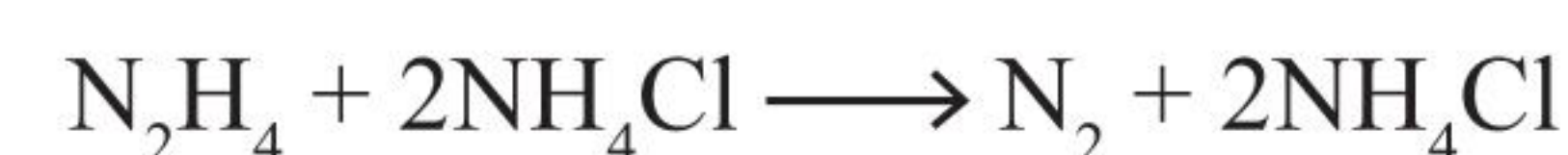
3. **Reaction with Nessler's reagent (test for ammonia):** Ammonia or ammonium salts reacts with Nessler's reagent to give a brown ppt. due to the formation of **iodide of Millon's base**.



4. **Reaction with sodium hypochlorite:** When an excess of ammonia solution is boiled with sodium hypochlorite, NaOCl in presence of glue or gelatin, hydrazine is formed.



Glue or gelatin catalyses the slow reaction and prevents the side reaction of the oxidation of hydrazine to nitrogen.



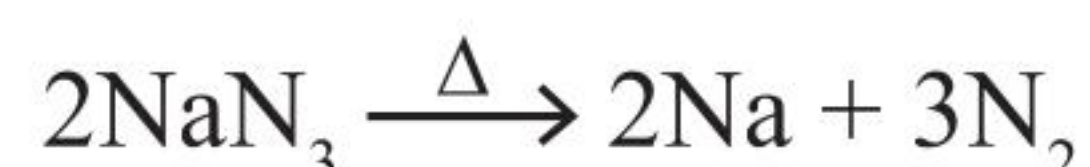
Uses:

1. To produce various nitrogenous fertilisers such as ammonium nitrate, urea, ammonium phosphate, ammonium sulphate, calcium ammonium nitrate (CAN) etc.
2. In the manufacture of some inorganic nitrogen compounds such as nitric acid (**in Ostwald's process**).
3. As a cleansing agent for removing grease.
4. Liquid ammonia is used as a refrigerant.
5. As a laboratory reagent.

ILLUSTRATION 2.6

- Write the reaction of thermal decomposition of sodium azide.
- Why does NH_3 act as a Lewis base?

Sol. a. Thermal decomposition of sodium azide, NaN_3 gives N_2 gas.



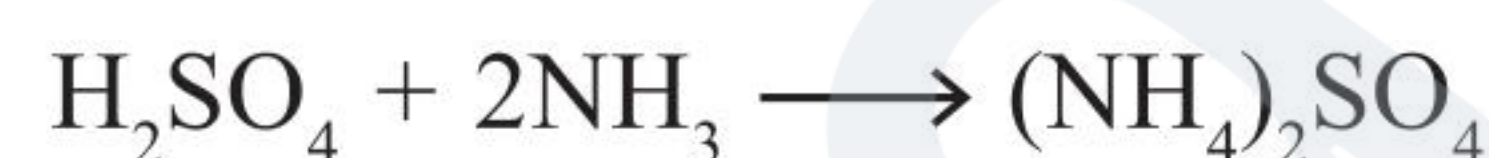
- Lone pair on N in NH_3 is present in one of the sp^3 hybridised orbital, due to the directional nature of lone-pair of electron on which is available for donation, NH_3 acts as a Lewis base.

ILLUSTRATION 2.7

- A bottle of liquor ammonia should be cooled before opening. Give reason.
- Why conc. H_2SO_4 , anhydrous CaCl_2 and P_4O_{10} cannot be used as dehydrating agents for ammonia.

Sol.

- Liquor ammonia has high vapour pressure at room temperature. Hence, to reduce the vapour pressure inside the bottle in order to avoid bumping, it has to be cooled.
- Conc. H_2SO_4 , anhydrous CaCl_2 and P_4O_{10} react with ammonia and hence do not behave as dehydrating agent.

**2.9 OXIDES OF NITROGEN**

Oxides of nitrogen provide a fascinating picture from the point of view of their varied structures and diverse chemical behaviour. They range from N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5 . The preparative routes for oxides of nitrogen and their properties are given in following Table 2.3.

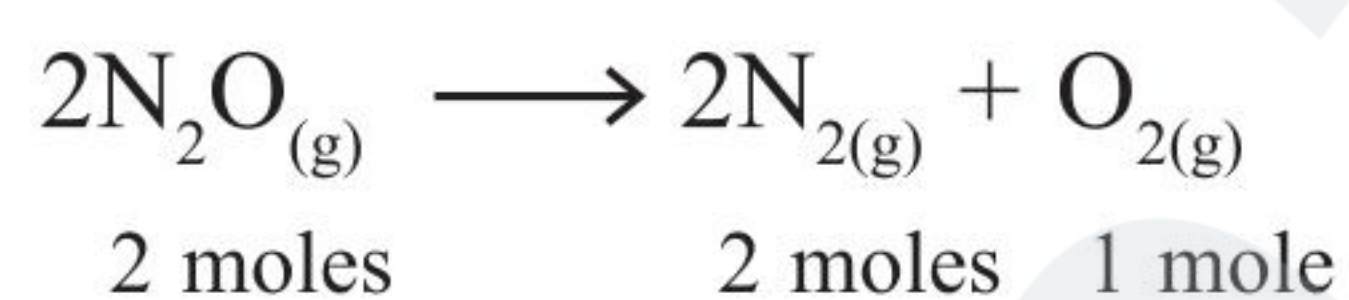
Table 2.3 Preparation and properties of oxides of nitrogen.

Name	Formula	Oxidation state of nitrogen	Preparation	Properties
Dinitrogen monoxide OR Nitrous oxide OR (Laughing gas)	N_2O	+1	$\text{NH}_4\text{NO}_3 \xrightarrow{250^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$ $\text{NH}_2\text{OH} + \text{HNO}_2 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$ $\text{Zn} + \text{dil. HNO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	- Colourless, neutral gas - In solid state, exist as $\text{N}_2\text{O} \cdot 6\text{H}_2\text{O}$ $2\text{N}_2\text{O} \xrightarrow{600^\circ\text{C}} 2\text{N}_2 + \text{O}_2$
Nitrogen monoxide or Nitric oxide	NO	+2	$\left[\begin{array}{l} \text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^- \\ 3e^- + \text{NO}_3^- \longrightarrow \text{NO} \end{array} \right]$ $3\text{Cu} + 8\text{HNO}_3(\text{dil}) \longrightarrow 2\text{NO} + 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$ - Catalytic oxidation of NH_3 $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$	- Colourless gas, solid and liquid NO is blue in colour. $2\text{NO} \xrightarrow{1100^\circ\text{C}} \text{N}_2 + \text{O}_2$ $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
Dinitrogen trioxide	N_2O_3	+3	$\text{NO} + \text{NO}_2 \longrightarrow \text{N}_2\text{O}_3$ $\text{As}_2\text{O}_3 + \text{HNO}_3(\text{dil}) + 2\text{H}_2\text{O} \longrightarrow \text{N}_2\text{O}_3 + 2\text{H}_3\text{AsO}_4$	- In solid and liquid state N_2O_3 is blue in colour. In gaseous state, N_2O_3 completely dissociates to give NO and NO_2. $\text{N}_2\text{O}_{3(\text{g})} \longrightarrow \text{NO} + \text{NO}_2$ - In conc. H_2SO_4, blue colour disappears due to formation of nitrosonium hydrogen sulphate. $\text{N}_2\text{O}_3 + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow 2\text{NO}^+ + 3\text{HSO}_4^- + \text{H}_3\text{O}^+$ - In presence of moisture, blue colour disappears due to formation of nitrous acid.
				$\text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_2$ Hence in aqueous medium N_2O_3 is acidic in nature.

Nitrogen dioxide	NO ₂	+4	$\left[\begin{array}{l} \text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^- \\ \text{NO}_3^- + e^- + \longrightarrow \text{NO}_2 \end{array} \right]$ 1. $\text{Cu} + 4\text{HNO}_3(\text{conc.}) \longrightarrow 2\text{NO}_2 + \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$ 2. $\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$ (LiNO₃ and Mg(NO₃)₂ also give same reaction.) 3. $\text{NO} + \text{O}_2 \longrightarrow \text{NO}_2$	1. NO₂ is a brown gas, highly reactive and paramagnetic. 2. Acts as an oxidising agent $2\text{Cu} + \text{NO}_2 \longrightarrow \text{CuO} + \text{NO}$ $2\text{C} + 2\text{NO}_2 \longrightarrow 2\text{CO}_2 + \text{N}_2$ $\text{X}_2 + 2\text{NO}_2 \longrightarrow 2\text{XNO}_2$ (X = Cl, Br) 3. With strong oxidising agents, higher oxides of N are formed. $\text{O}_3 + 2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_5 + \text{O}_2$
Nitrogen tetroxide	N ₂ O ₄	+4	$2\text{NO}_2 \xrightleftharpoons[\Delta]{\text{Cooling}} \text{N}_2\text{O}_4$	1. $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \longrightarrow \text{HNO}_2 + \text{HNO}_3$ 2. $\text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow \text{NO}^+\text{HSO}_4^- + \text{HNO}_3$ 3. Exists in equilibrium with NO both in gaseous and liquid state.
Dinitrogenpentoxide	N ₂ O ₅	+5	1. $2\text{HNO}_3 + \text{P}_2\text{O}_5 \longrightarrow 2\text{HPO}_3 + \text{N}_2\text{O}_5$ 2. $4\text{AgNO}_3 + 2\text{Cl}_2 \longrightarrow 4\text{AgCl} + 2\text{N}_2\text{O}_5 + \text{O}_2$	1. In solid state, exist as a crystalline ionic compound, [NO₂]⁺ [NO₃]⁻ i.e. nitronium nitrate In gaseous state, exist as N₂O₅ having as oxygen bridge, N–O–N 2. In solid or gaseous state exist as $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$ 3. $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$ That is why N₂O₅ is also known as anhydride of HNO₃. Hence it is acidic in nature.

2.9.1 DINITROGEN MONOXIDE OR NITROGEN (I) OXIDE (N₂O)

N₂O acts as better supporter of combustion than air. Reason being, in air % of O₂ is ≈ 22%, while N₂O decomposes to give ≈ 33% of O₂.



When inhaled in small amounts, N₂O induces intoxication and hysterical excitement often accompanied by convulsion laughter hence it is also known as **Laughing gas**. In large amounts, it acts as a narcotic. It is also used as an anaesthetic particularly in dentistry and gynaecology.

2.9.2 DINITROGEN OXIDE OR NITRIC OXIDE (NO)

Despite being odd electron the molecule is colourless. This can be explained on the basis of its electronic configuration.

NO (7 + 8 = 15 electrons)

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_y^2 = \pi 2p_x^2 < \pi^* 2p_y^1 < \pi^* 2p_x^0 < \sigma^* 2p_z^0$$

For NO to be coloured, transition from $\pi^* 2p \longrightarrow \sigma^* 2p$ is required which is forbidden, hence NO is colourless.

$$\text{B.O. of NO} = 1/2 (\text{N}_b - \text{N}_a) = 1/2 (10 - 5) = 2.5$$

NO⁺ will be more stable than NO molecule, as

$$\text{B.O. (NO}^+) = 1/2 (10 - 4) = 3.0$$

Bond order (B.O.) ∝ Stability

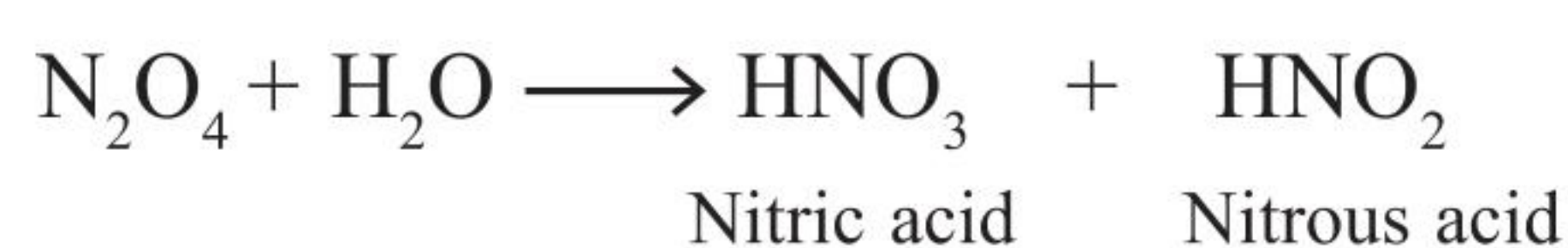
Greater the bond order, greater is the stability of the molecule.

In spite of its reactive and harmful nature, NO occurs in biological system in traces. **It acts as a neurotransmitter and plays a significant role in controlling blood pressure by relaxing blood vessels. It also provides protection from bacterial infections.**

Nitric oxide and nitrogen dioxide are important in the manufacture of nitric acid and nitrate fertilisers.

2.9.3 N₂O₄

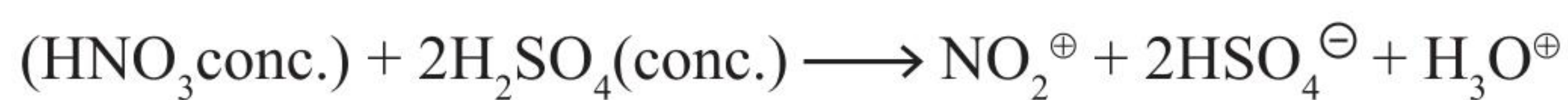
N₂O₄ is mixed anhydride of HNO₃ and HNO₂ as on reaction with water, N₂O₄ gives HNO₃ and HNO₂.



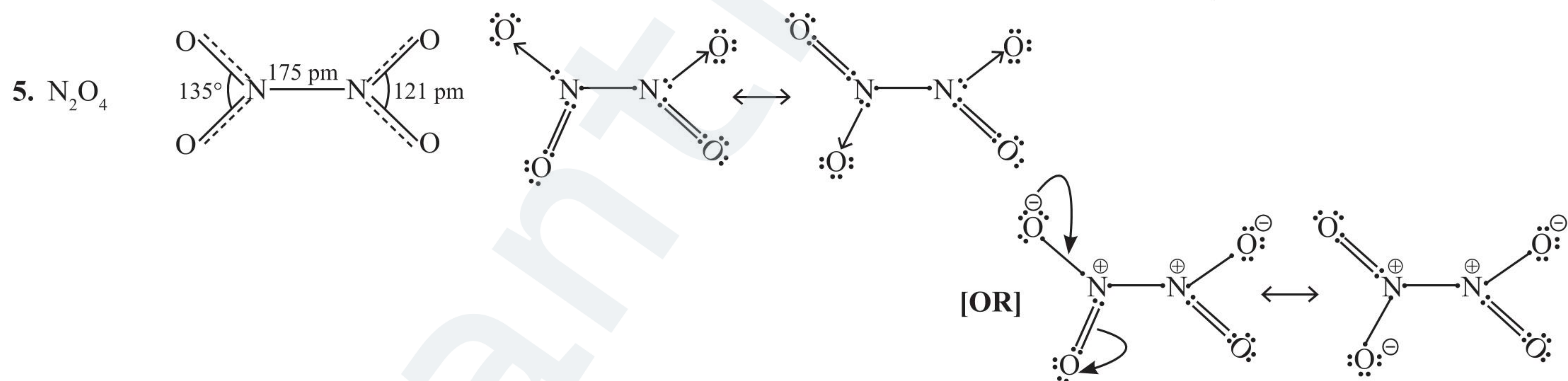
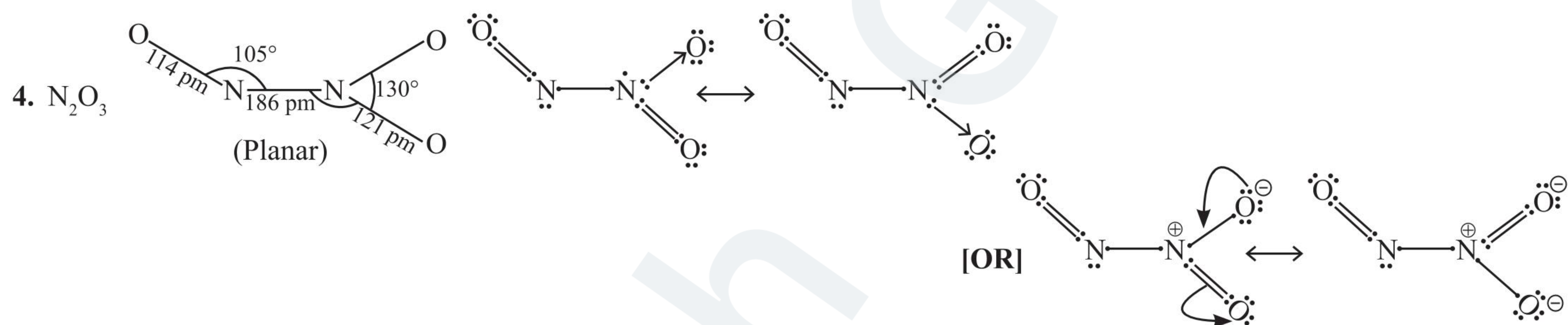
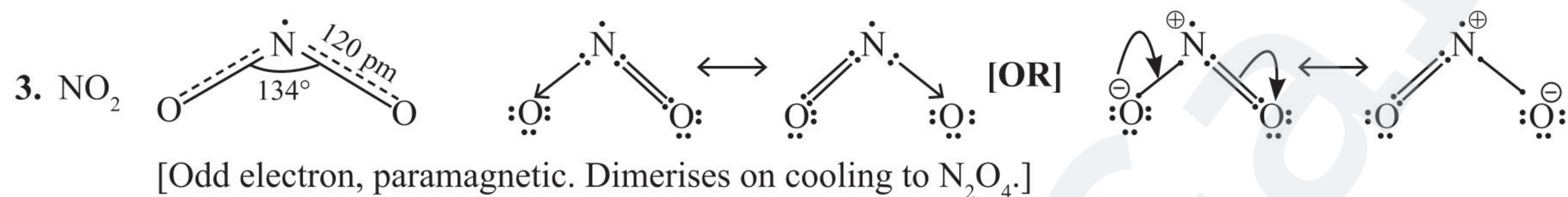
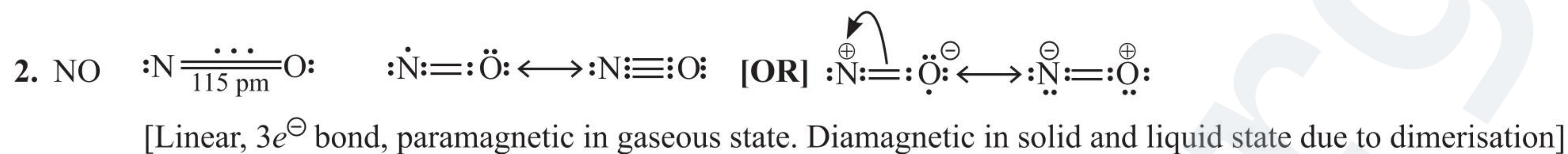
N₂O₄ is used as an oxidiser for rocket fuels in missiles and space vehicles.

2.9.4 NITRONIUM ION (NO_2^+)

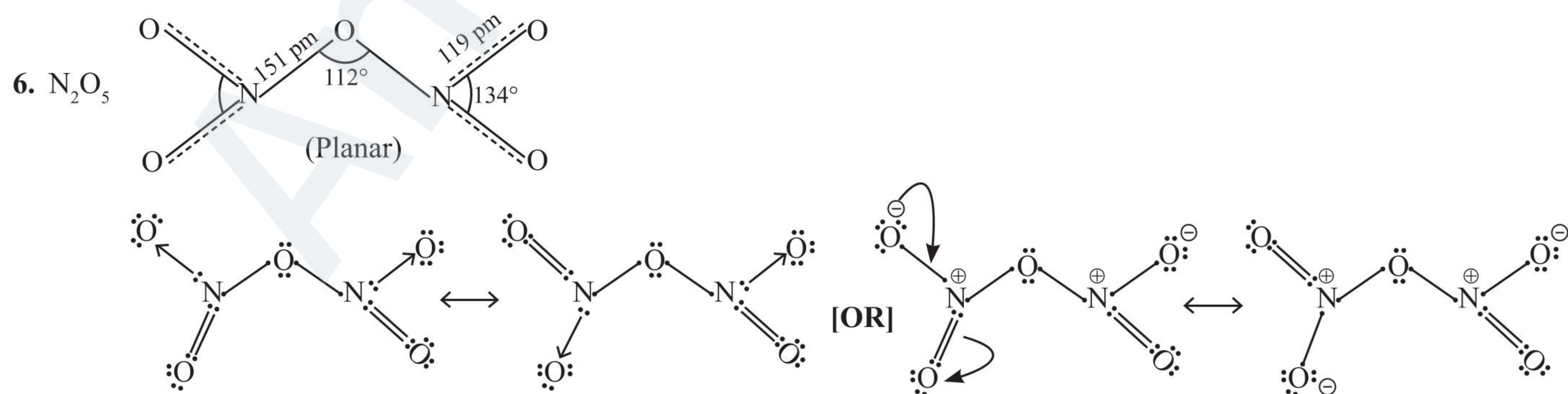
It is an active electrophilic species present in the mixtures of conc. H_2SO_4 and conc. HNO_3 used as a nitrating mixture in organic chemistry.



2.9.5 RESONATING STRUCTURE OF NITROGEN OXIDES



(Diamagnetic, dissociate on heating to NO_2)



[Solid N_2O_5 exists as $[\text{NO}_2]^+ [\text{NO}_3]^-$ and is called nitronium nitrate]

Fig. 2.4 Resonating structures of oxides of nitrogen

2.10 NITRIC ACID (HNO₃)

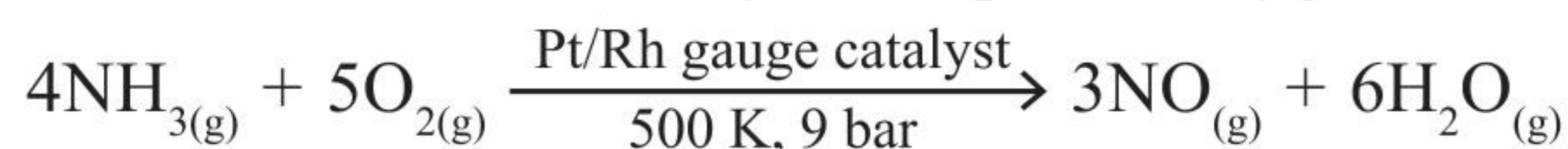
Nitric acid was named **aqua fortis** (meaning strong water) by Alchemists.

2.10.1 PREPARATION

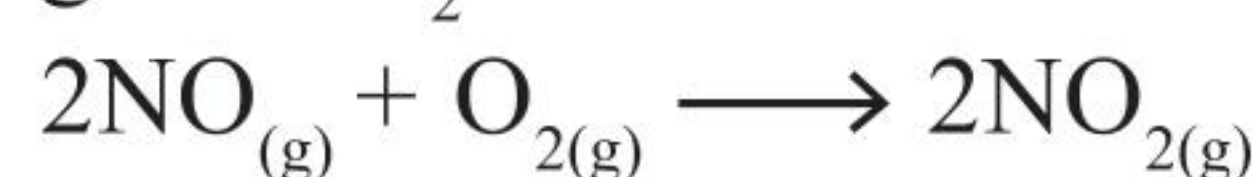
- In the laboratory:** Nitric acid is prepared by heating KNO₃ or NaNO₃ and concentrated H₂SO₄ in glass apparatus since HNO₃ attacks rubber and cork.



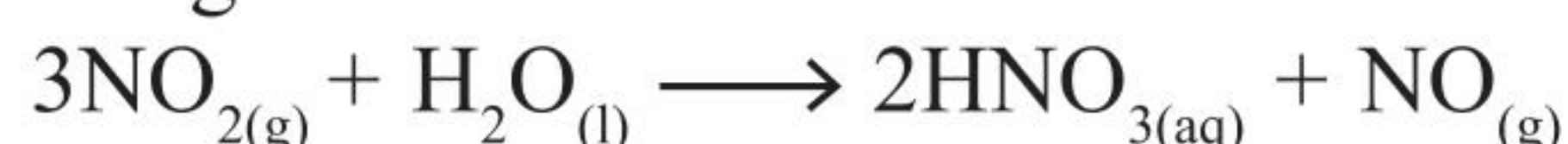
- On commercial scale:** It is manufactured mainly by **Ostwalds process**. This method is based upon the catalytic oxidation of ammonia by atmospheric oxygen.



Nitric oxide thus formed readily combines with oxygen to give NO₂



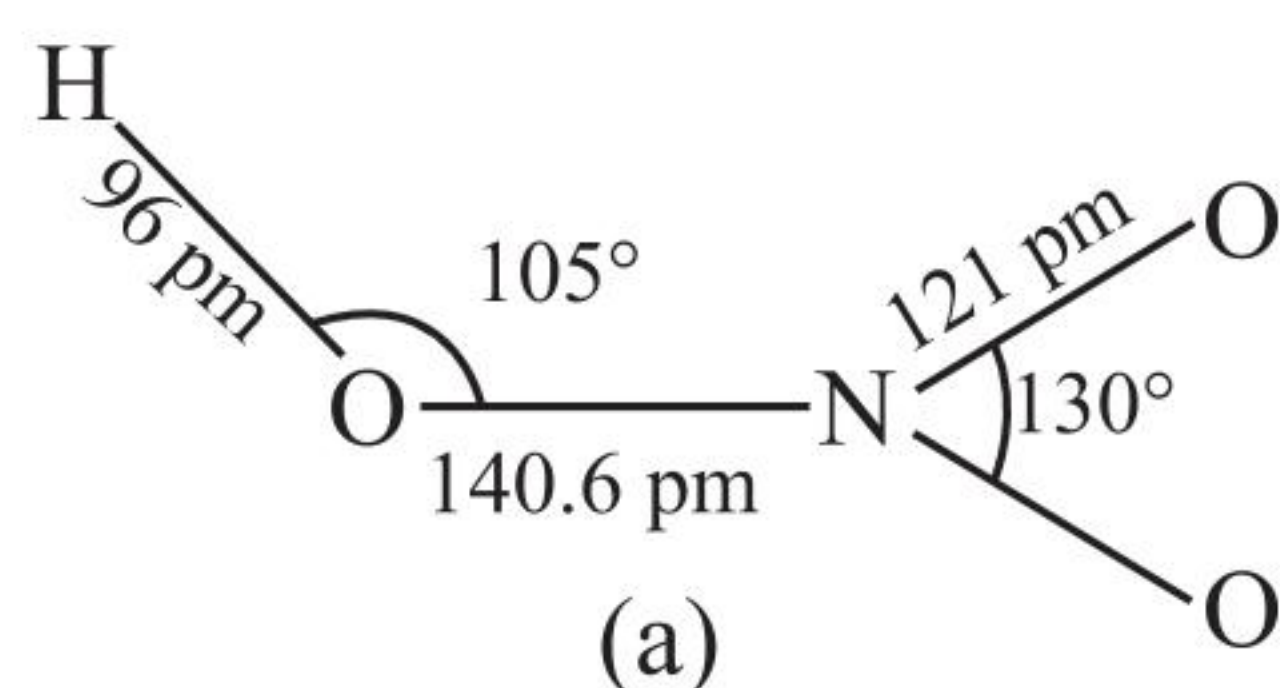
Nitrogen dioxide thus formed dissolves in water to form HNO₃.



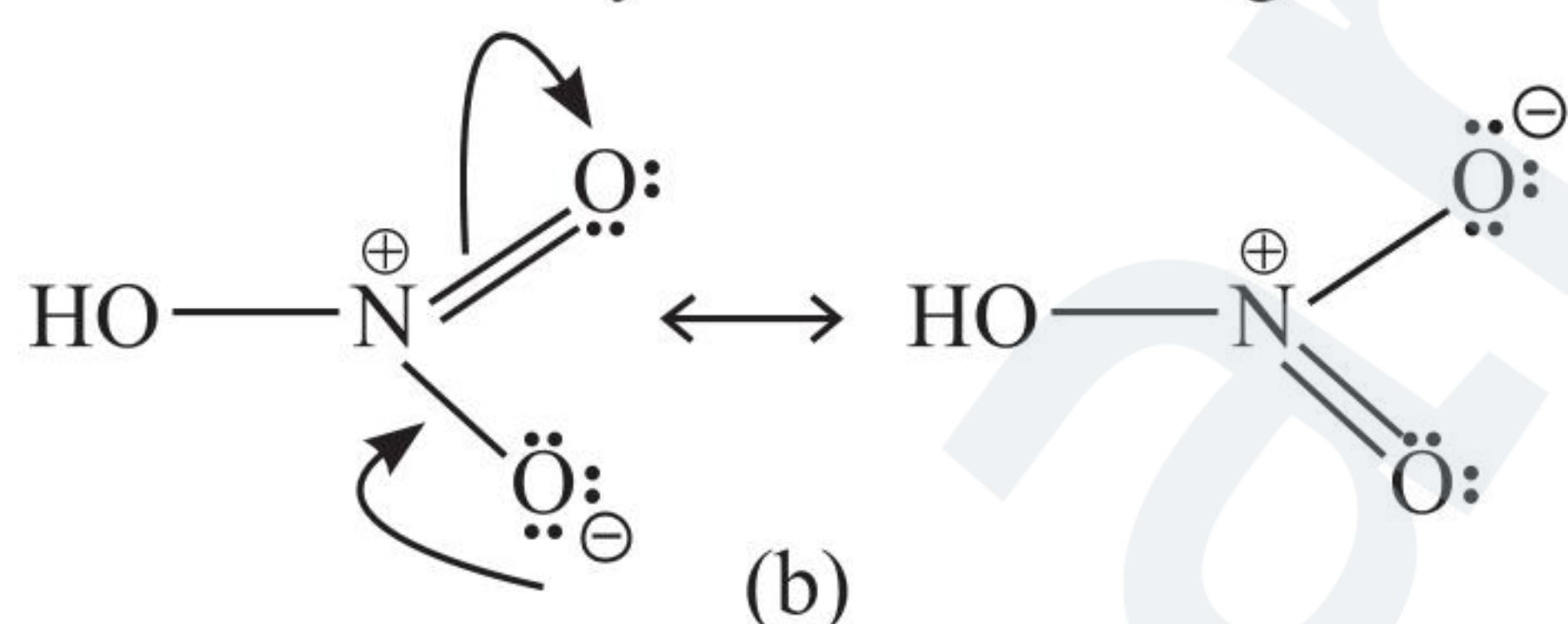
The nitric oxide thus formed is recycled and the aqueous HNO₃ is concentrated by distillation to give 68% HNO₃ by mass. (HNO₃ forms azeotrope at 68% HNO₃ and 32% water both by mass). Further concentration to 98% can be achieved by dehydration with concentrated H₂SO₄.

2.10.2 STRUCTURE

Spectroscopic studies have shown that in the gaseous state, HNO₃ exists as a planar molecule.



Nitric acid is a resonance hybrid of following:



2.10.5 REACTION OF DIFFERENT ELEMENT WITH HNO₃

These are summarised in Table 2.4.

Table 2.4 Reactions of different elements with HNO₃

Different concentration of nitric acid	Element	Main products
Conc. HNO ₃ (NO ₃ [⊖] + 2H [⊕] + e [⊖] → NO ₂ + H ₂ O) (‘n’ factor = 1)	Cu, Ag, Hg, Pb, Zn	Metal nitrate + NO ₂
	Fe, Al, Co, Ni, Cr	Rendered passive
	Sn	Metastannic acid or hydrated stannic oxide (H ₂ SnO ₃) and NO ₂
Moderately conc. HNO ₃	Fe	Ferric nitrate and NO ₂
Dilute HNO ₃ 4H [⊕] + NO ₃ [⊖] + 3e [⊖] → NO + 3H ₂ O (‘n’ factor = 3)	Cu, Ag, Hg, Pb	Metal nitrates and NO
	a. More active metals with dil. HNO ₃ like Zn, Fe, Sn b. 2NO ₃ [⊖] + 10H [⊕] + 8e [⊖] → N ₂ O + 5H ₂ O (‘n’ factor = 8/2 = 4)	Metal nitrates and N ₂ O

2.10.3 PHYSICAL PROPERTIES

- Pure HNO₃ is colourless liquid with pungent odour (freezing point 231.4 K and boiling point 355.6 K). However, impure HNO₃ is yellow due to the presence of dissolved NO₂.
- Laboratory grade HNO₃ contains ~ 68% of the HNO₃ by mass and has specific gravity of 1.504.
- Fuming nitric acid** is pure nitric acid with dissolved NO₂ in it.

2.10.4 CHEMICAL PROPERTIES

- On heating, HNO₃ decomposes to give nitrogen dioxide, oxygen and water.



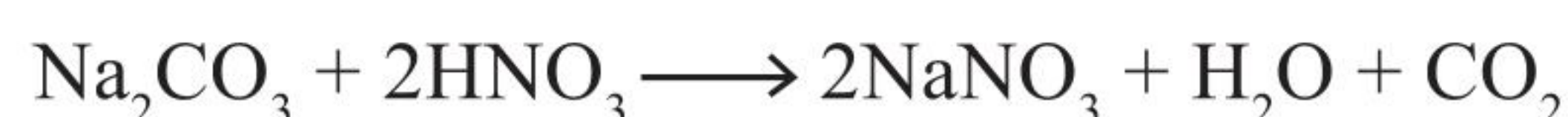
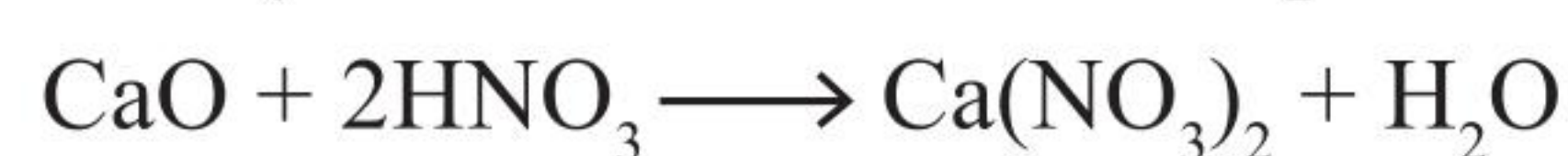
- Nitric acid is stored in brown coloured gas bottles, to prevent photochemical decomposition of HNO₃.



- HNO₃ behaves as strong monobasic acid and ionises as follows:



It reacts with basic oxides, carbonates, bicarbonates and hydroxides to form corresponding salts.



- Oxidising nature:** Nitric acid acts as strong oxidising agent as it decomposes to give nascent oxygen easily.



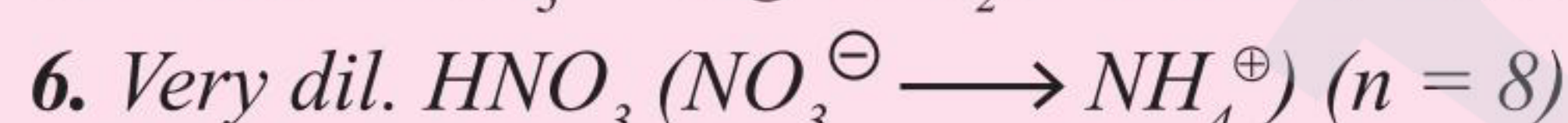
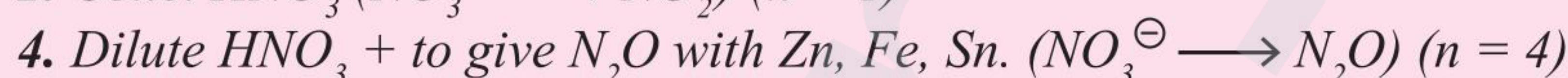
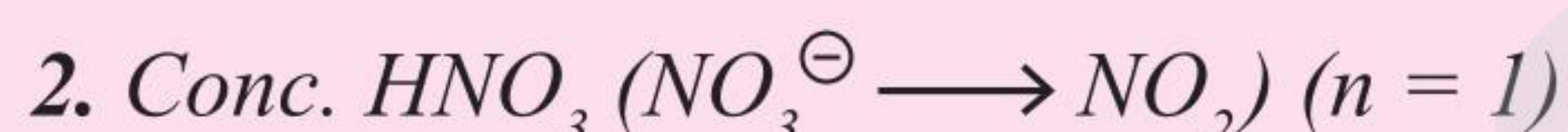
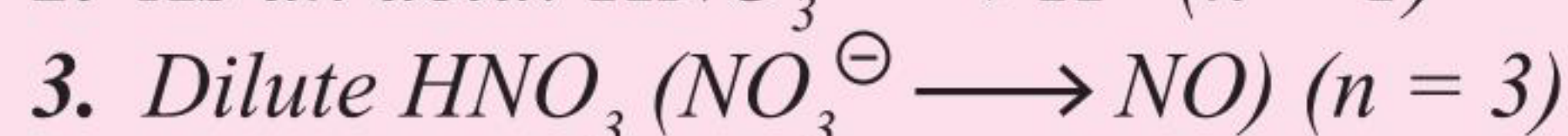
or



Most of the metals except noble metals like Au and Pt react with HNO₃. **Some metals like Fe, Al, Co, Ni and Cr do not dissolve in conc. HNO₃ because of the formation of a layer of oxide on the metal surface, thus these metals are rendered passive.**

1. Very dil. HNO_3 $10\text{H}^{\oplus} + 8\text{e}^{\ominus} + \text{NO}_3^{\ominus} \longrightarrow \text{NH}_4^{\oplus} + 3\text{H}_2\text{O}$ (‘n’ factor = 8)	More active metals Zn, Fe, Sn	Metal nitrates and hydroxylamine (NH_2OH) or $\text{NH}_4^{\oplus}$ ion or ammonium nitrate (NH_4NO_3)
2. Cold dil. HNO_3 $7\text{H}^{\oplus} + 6\text{e}^{\ominus} + \text{NO}_3^{\ominus} \longrightarrow \text{NH}_2\text{OH} + 2\text{H}_2\text{O}$ (‘n’ factor = 6)	Mg, Mn	Metal nitrates and H_2
Aqua regia (conc. HCl : conc. HNO_3 = 3 : 1)	Noble metals like Au, Pt	Complex ions such as $[\text{AuCl}_4]^{\ominus}$, $[\text{PtCl}_6]^{2-}$ and $\text{NO}_{(\text{g})}$

Note: ‘n’ factor for different concentration of HNO_3



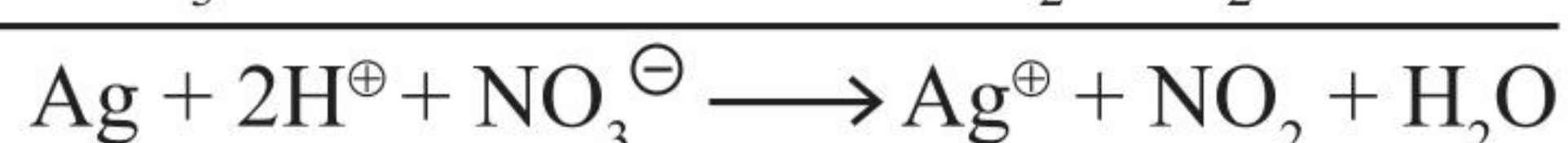
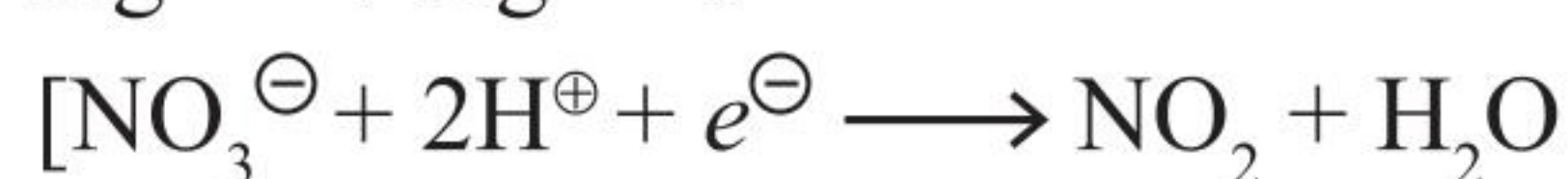
(A) Reactions with conc. HNO_3

i. Cu, Ag, Hg, Pb, Zn react with conc. HNO_3 to form metal nitrates, and $\text{NO}_3^{\ominus}$ is reduced to NO_2 .



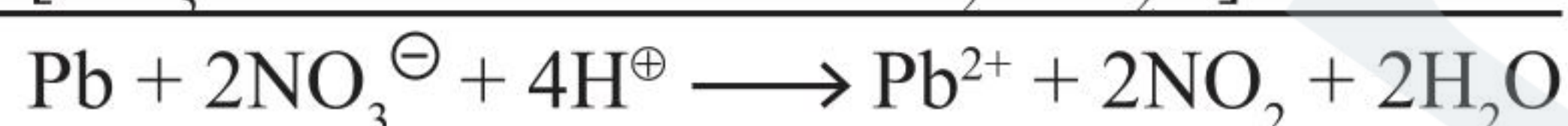
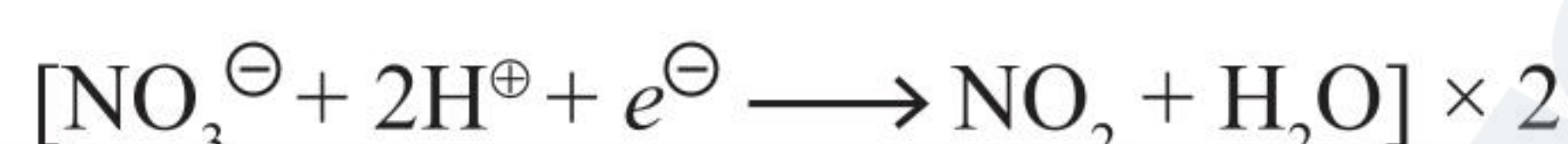
Add $2\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation
or $\text{Cu} + 4\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

ii. ($\text{Ag} \longrightarrow \text{Ag}^{\oplus} + \text{e}^{\ominus}$, $\text{NO}_3^{\ominus} + \text{e}^{\ominus} \longrightarrow \text{NO}_2$)



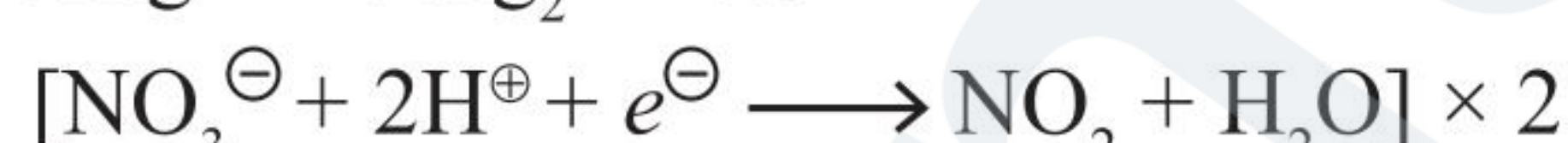
Add $2\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation
or $\text{AgNO}_3 + 2\text{HNO}_3 \longrightarrow \text{AgNO}_3 + \text{NO}_2 + \text{H}_2\text{O}$

iii. ($\text{Pb} \longrightarrow \text{Pb}^{2+} + 2\text{e}^{\ominus}$, $\text{NO}_3^{\ominus} + \text{e}^{\ominus} \longrightarrow \text{NO}_2$)



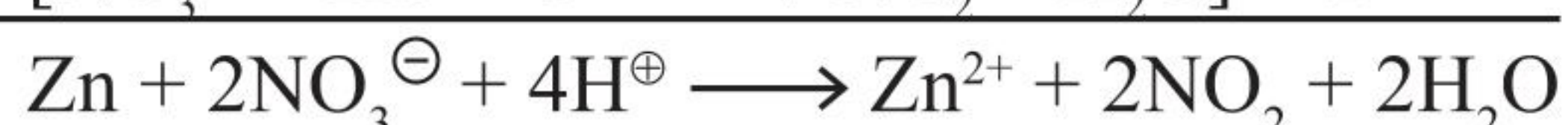
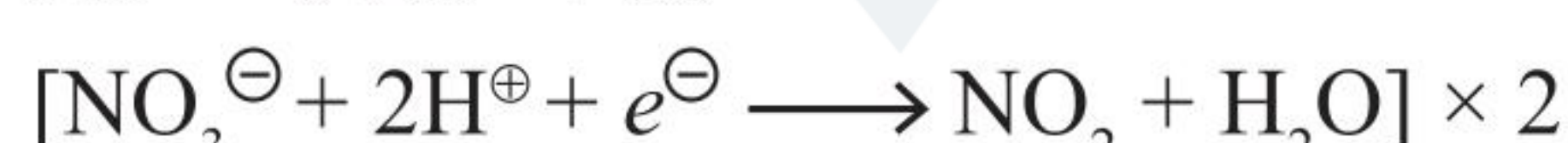
Add $2\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation
or $\text{Pb} + 4\text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

iv. ($2\text{Hg} \longrightarrow \text{Hg}_2^{2+}$, $\text{NO}_3^{\ominus} \longrightarrow \text{NO}_2$)



Add $2\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation
or $2\text{Hg} + 4\text{HNO}_3 \longrightarrow \text{Hg}_2(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O}$

v. ($\text{Zn} \longrightarrow \text{Zn}^{2+}$, $\text{NO}_3^{\ominus} \longrightarrow \text{NO}_2$)

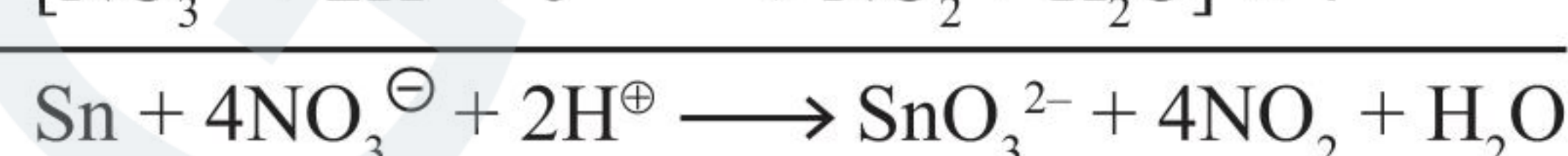
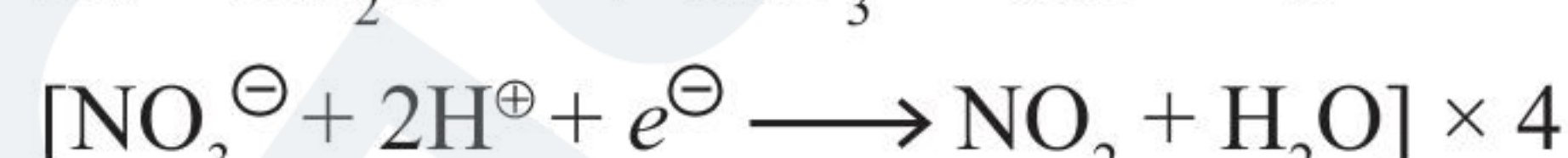


Add $2\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation
or $\text{Zn} + 4\text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

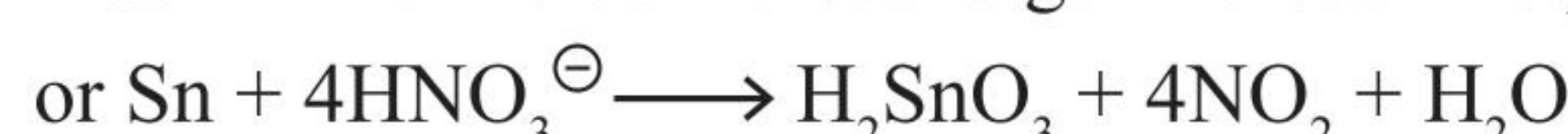
(B) Fe, Al, Co, Ni and Cr are rendered passive with conc. HNO_3 . The inertness exhibited by metals under conditions in which chemical activity is expected is known as passivity. A thin

layer of oxide is formed on Fe, Al, Co, Ni and Cr with conc. HNO_3 , which prevents the further action of conc. HNO_3 .

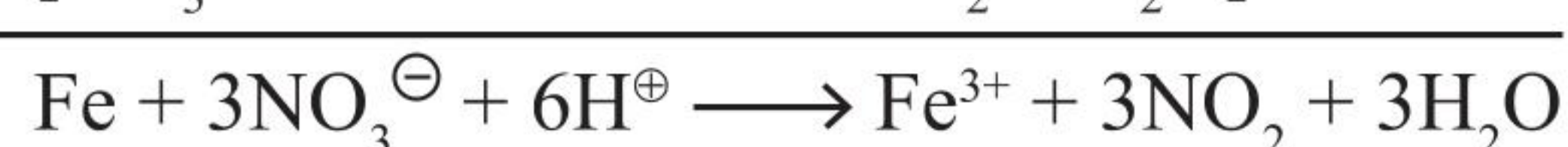
(C) Sn is oxidised to metastannic acid



Add $2\text{H}^{\oplus}$ ion to both sides to get molecular equation



(D) With moderately conc. H_2SO_4 , Fe gives ferric nitrate, HNO_3 is reduced to NO_2 .

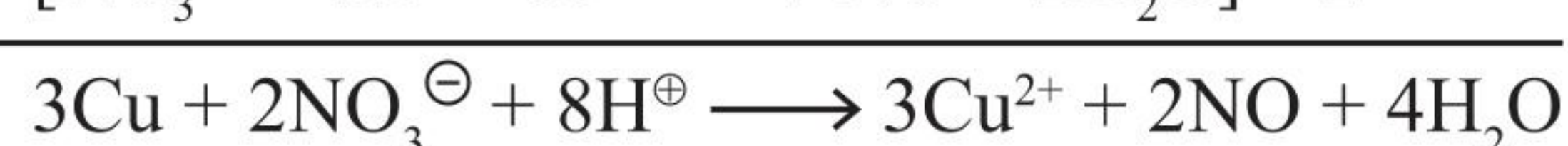
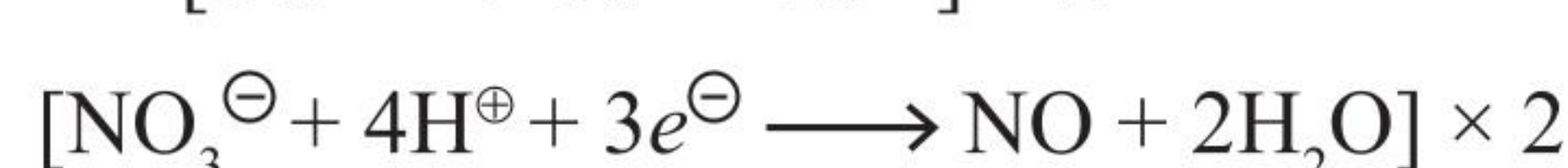
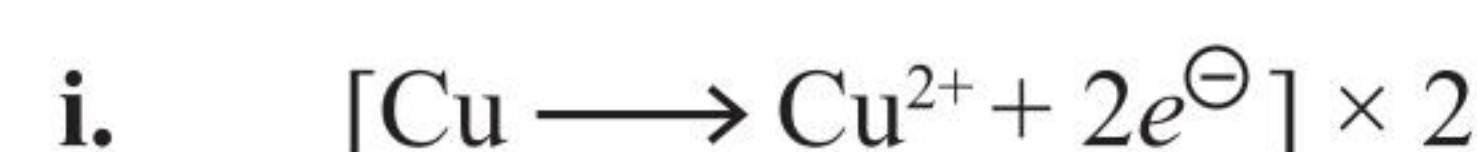


Add $3\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation

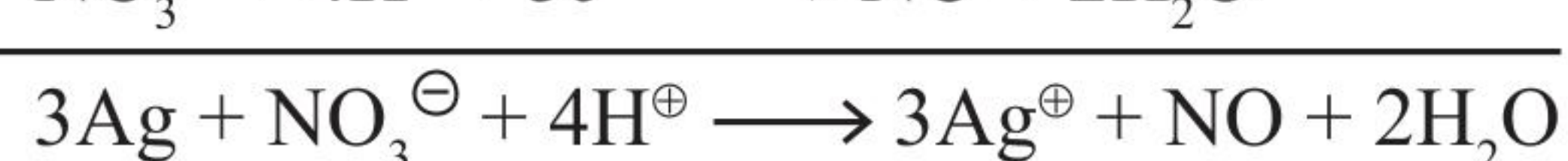
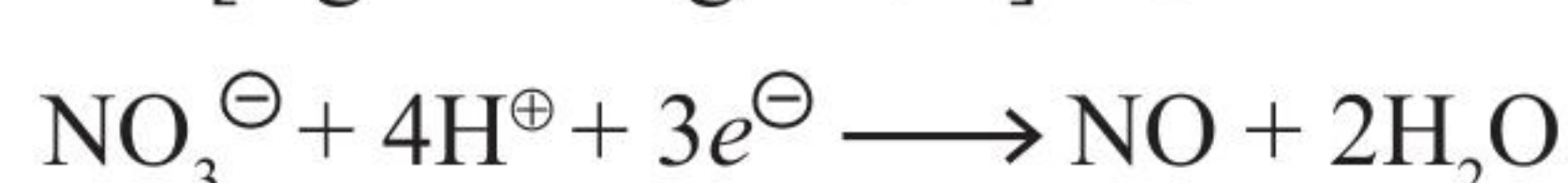
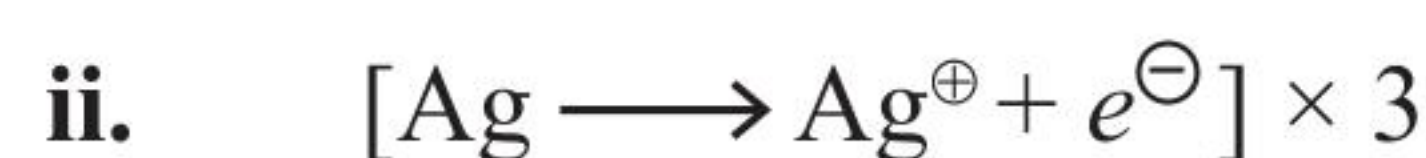


(E) With dil HNO_3 :

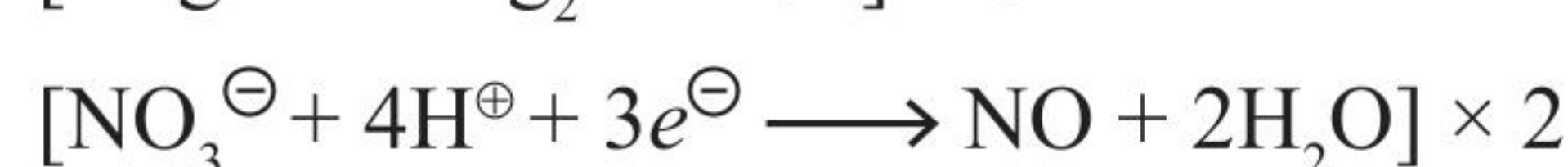
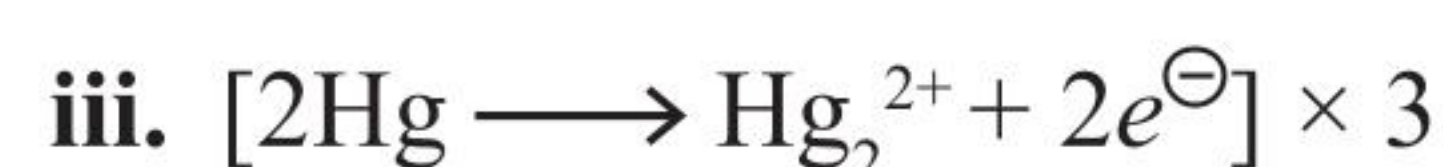
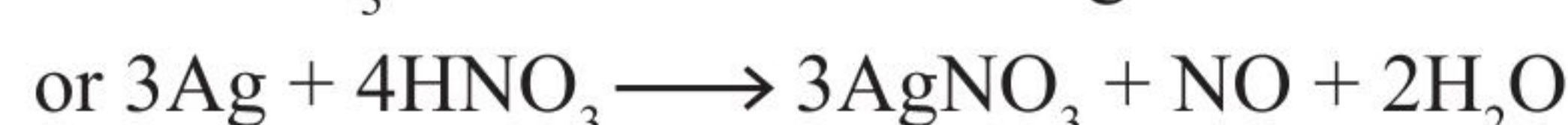
I. Cu, Ag, Hg, Pb reacts with dil. HNO_3 to give metal nitrate and HNO_3 is reduced to NO.



Add $6\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation

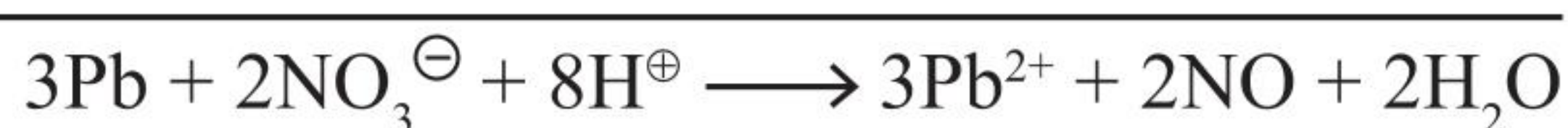
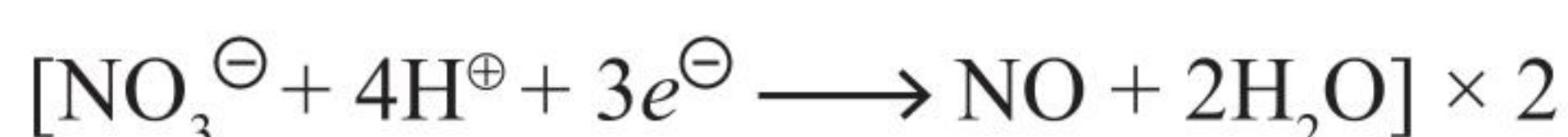


Add $3\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation



Add $6\text{NO}_3^{\ominus}$ ion to both sides to get molecular equation



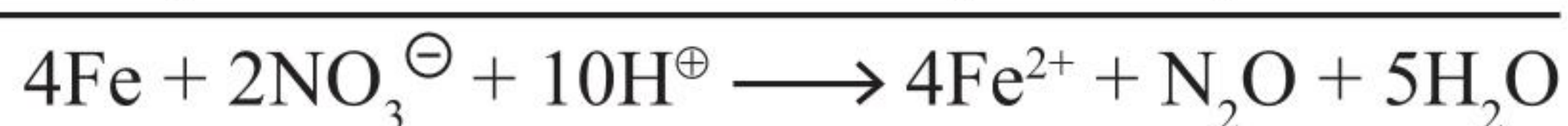


Add 6NO_3^- ion to both sides to get molecular equation
or $3\text{Pb} + 8\text{HNO}_3 \longrightarrow 3\text{Pb}_2(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

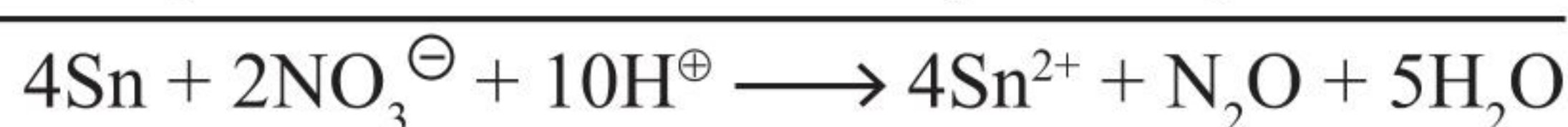
II. Zn, Fe, and Sn reacts with dil. HNO_3 to form metal nitrates and HNO_3 is reduced to N_2O .



Add 8NO_3^- ion to both sides to get molecular equation
or $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$



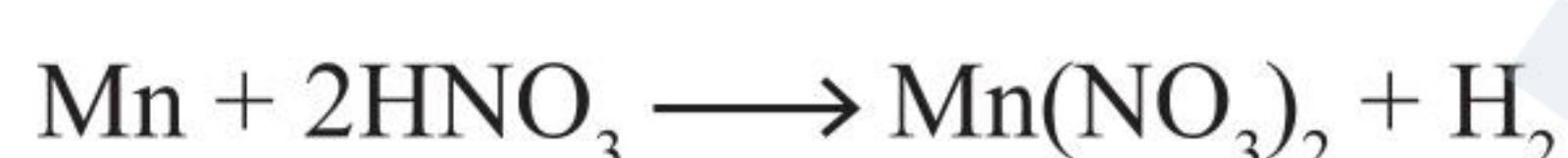
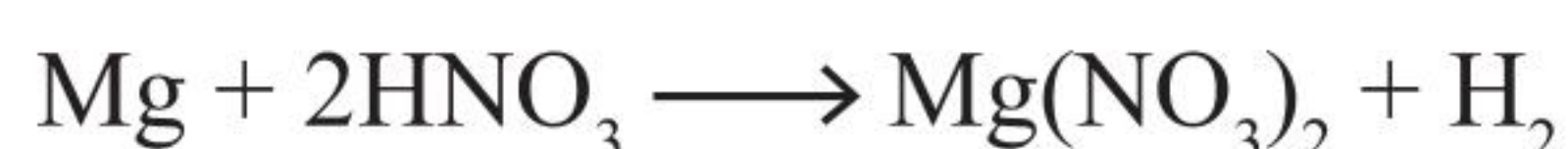
Add 8NO_3^- ion to both sides to get molecular equation
or $4\text{Fe} + 10\text{HNO}_3 \longrightarrow 4\text{Fe}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$



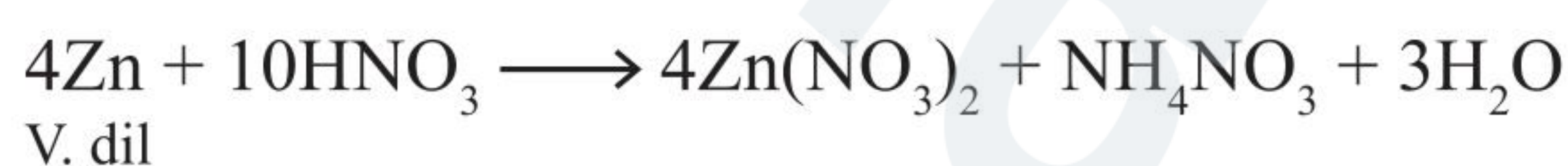
Add 8NO_3^- ion to both sides to get molecular equation
or $4\text{Sn} + 10\text{HNO}_3 \longrightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$

(F) With very dil. HNO_3 :

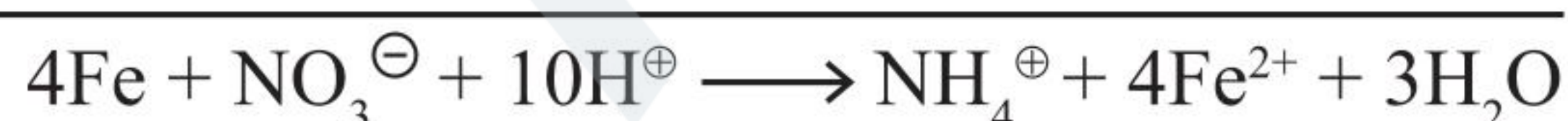
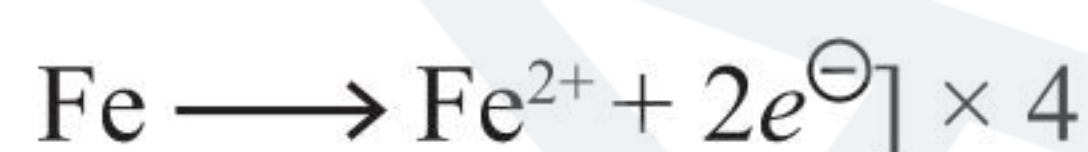
i. Mg and Mn liberate H_2



ii. Zn, Fe and Sn form metal nitrates and hydroxylamine or ammonium nitrate

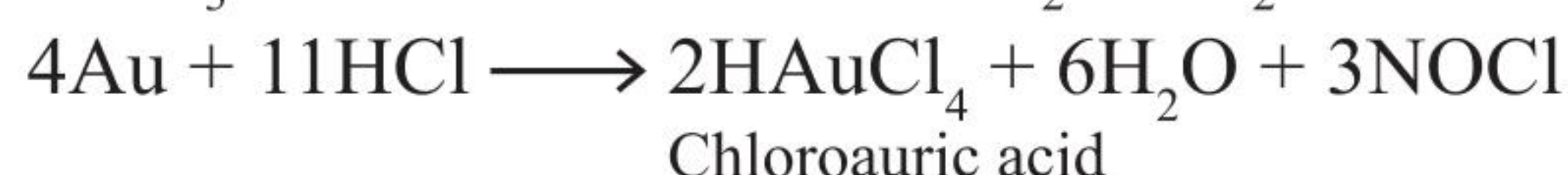


Ionic equation:

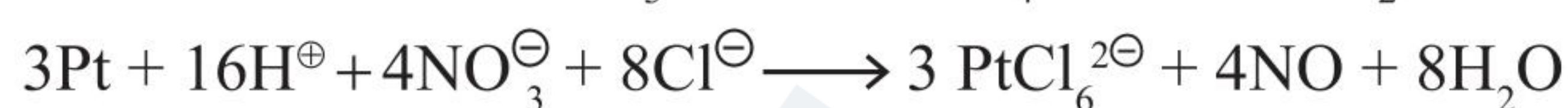
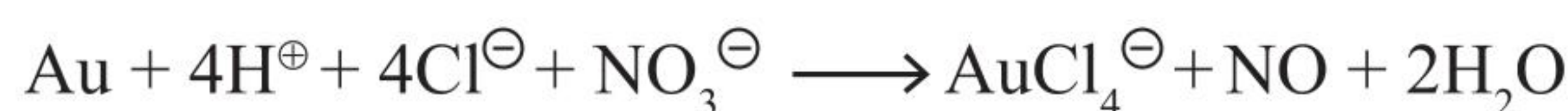


Add 9NO_3^- ion to both sides to get molecular equation.
Similarly, ionic equation for Sn and Zn can be written.

(G) Noble metals like gold, platinum, iridium, rhodium etc. do not react in HNO_3 . However, these metals dissolve in aqua regia (3 parts of conc. HCl and one part of conc. HNO_3) due to formation of chlorocomplexes such as AuCl_4^- , PtCl_6^{2-} etc.



Ionic equations:

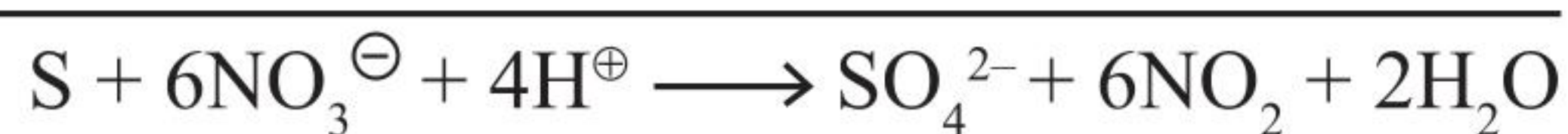
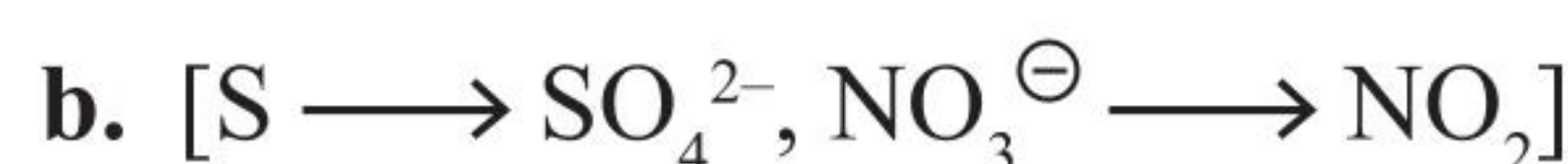
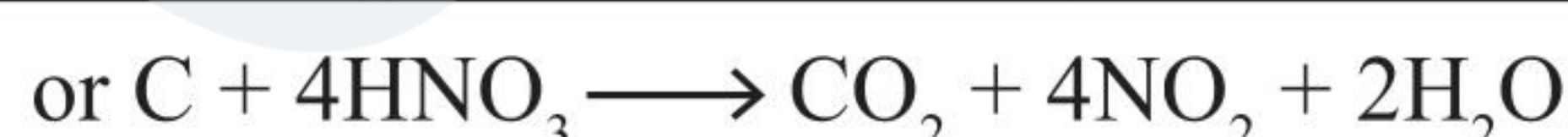
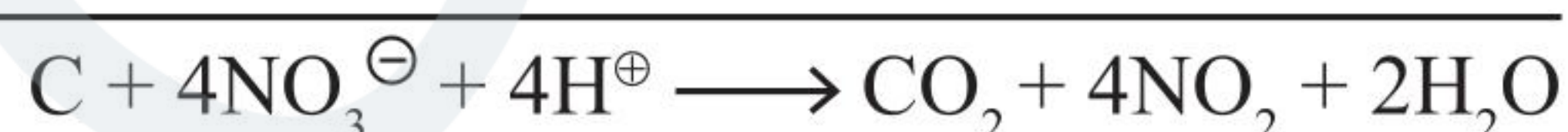
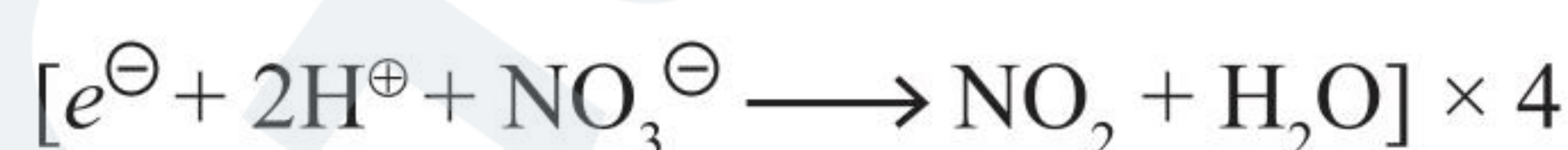


i. Cane sugar is oxidised to oxalic acid on reacting with HNO_3 .

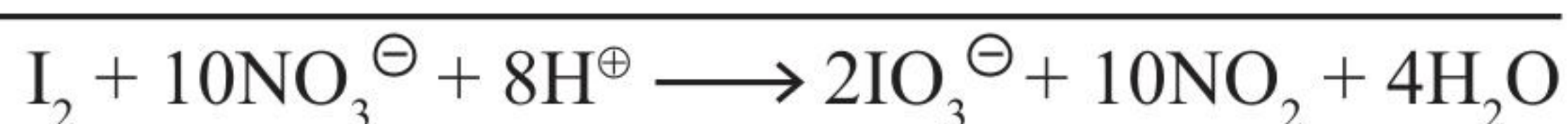


ii. Nitric acid reacts with proteins forming **xanthoprotein**, a yellow nitro compound. It therefore stains skin and renders wool yellow. This property is used for the test of proteins.

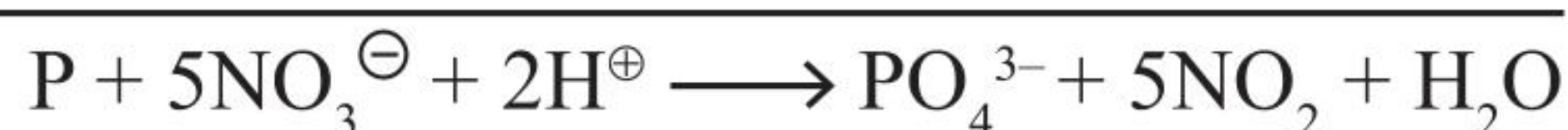
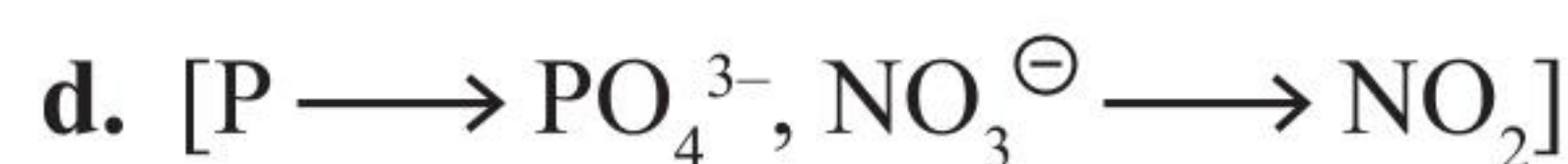
iii. **Oxidation of non-metals:** Dilute HNO_3 does not react with non-metals. But conc. HNO_3 oxidises non-metals such as C, S, I and metalloids such as As, Sb, etc. to their corresponding oxyacids, while nitric acid is reduced to NO_2 .



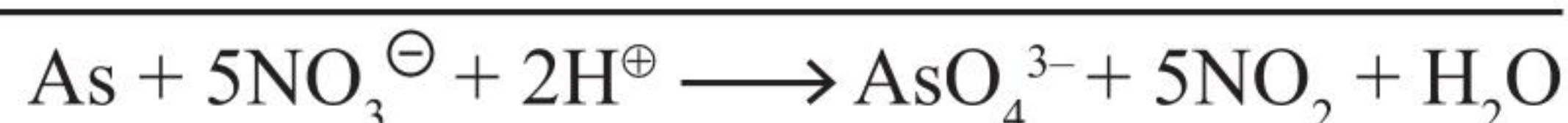
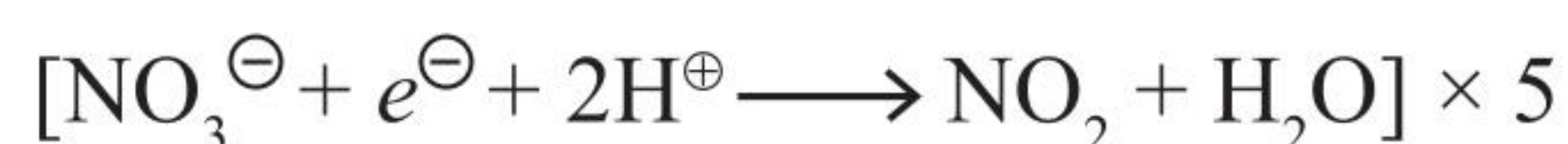
Add 2H^+ ion to both sides to get molecular equation
or $1/8 \text{S}_8 + 6\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$



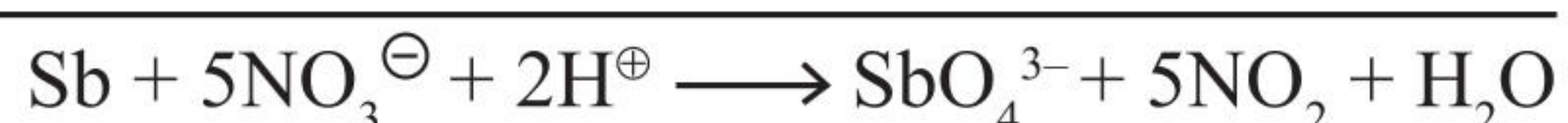
Add 2H^+ ion to both sides to get molecular equation
or $\text{I}_2 + 10\text{HNO}_3 \longrightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$



Add 3H^+ ion to both sides to get molecular equation
or $1/4 \text{P}_4 + 5\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$



Add 3H^+ ion to both sides to get molecular equation
or $\text{As} + 5\text{HNO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$



Add 3H^+ ion to both sides to get molecular equation

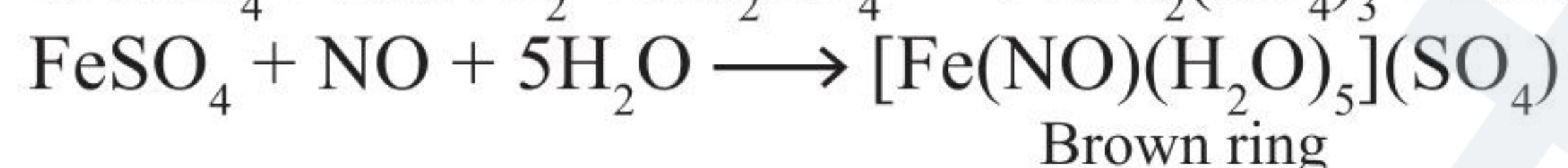
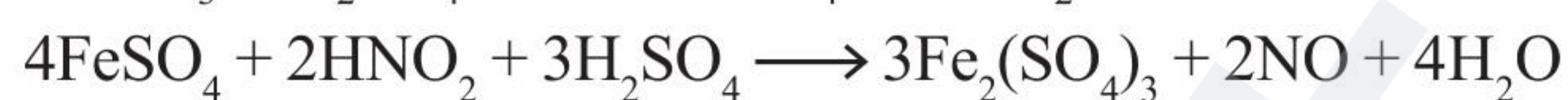
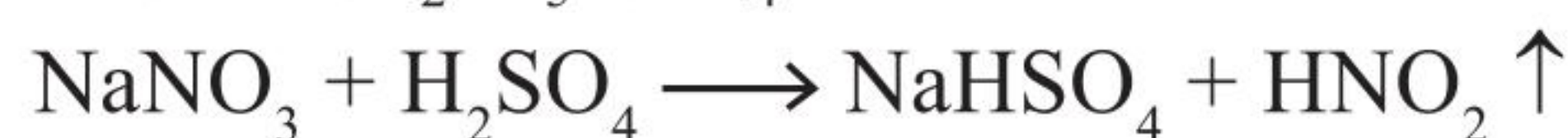


2.10.6 USES OF NITRIC ACID

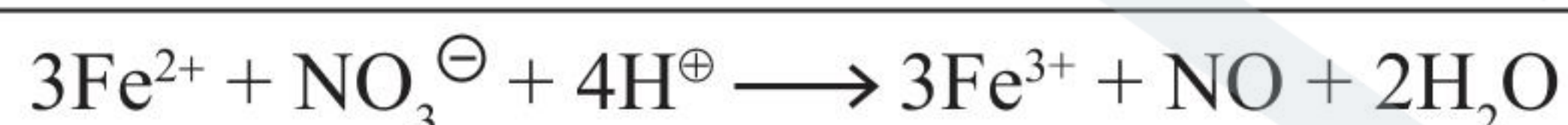
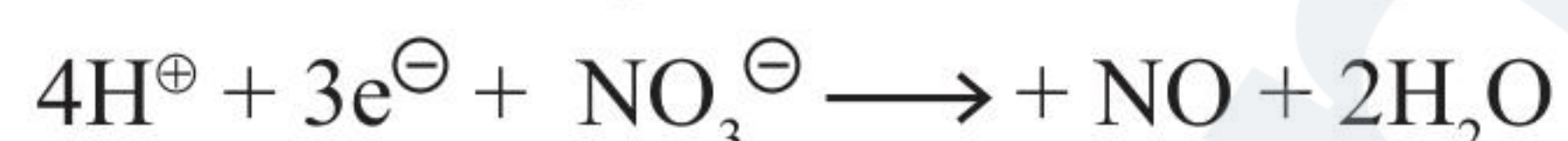
1. For purification of Au and Ag.
2. In the manufacture of TNT (trinitrotoluene), nitroglycerine and other organic nitro compounds.
3. In the pickling of stainless steel.
4. In etching of metals and as an oxidiser in rocket fuel.
5. In the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.

2.10.7 TEST OF NITRATE ION (BROWN RING TEST)

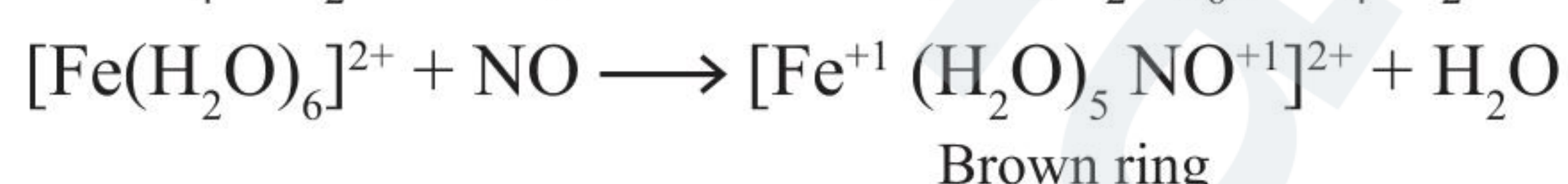
1. $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ ion is formed in the brown ring test for the confirmation of nitrate ion in the salt analysis. To the nitrate solution, equal volume of freshly prepared saturated solution of FeSO_4 is added. To this solution, conc. H_2SO_4 is added slowly from the side of the test tube so that acid forms a layer beneath the mixture. A brown ring is formed at the junction of the two liquids, due to formation $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5](\text{SO}_4)$.



Ionic equations for NO_3^- ion test is represented as:-



$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is represented as $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$



2. The complex is paramagnetic ($n = 3$) and

$$\mu = \sqrt{15} = 3.83 \text{ BM.}$$

2.11 ALLOTROPY

Allotropy is the phenomenon by which an element exists in two or more different crystalline or amorphous forms; and the different forms are called allotropic forms or allotropes of the given element. Different allotropic forms of an element have different physical properties but similar chemical properties.

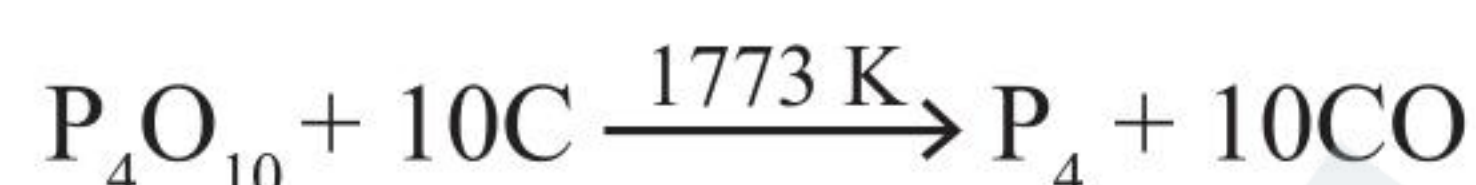
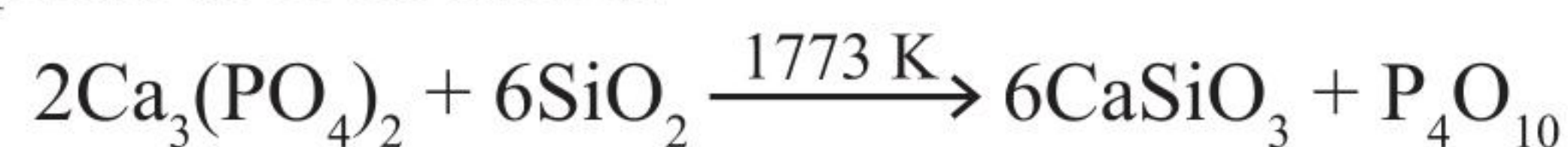
2.11.1 ALLOTROPIC FORMS OF PHOSPHOROUS

Phosphorous is found in various allotropic forms or modifications. Some important allotropes of phosphorous are:

1. White or yellow phosphorous
2. Red phosphorous
3. Black phosphorous

2.11.1.1 White Phosphorous

Preparation: On heating, phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$ with coke and sand in an electric furnace at 1773 K, white or yellow phosphorous is obtained.



Structure: White phosphorous exists as tetrahedra tetraatomic discrete P_4 units (Fig. 2.10). The four phosphorous atoms are sp^3 hybridised and lie at the corners of the regular tetrahedron. Each phosphorous atom is linked to each of the other three atoms by covalent bonds. The P-P bond length is equal to 221 pm, and $\angle \text{PPP} = 60^\circ$. Due to high angular strain, white phosphorous is highly reactive.

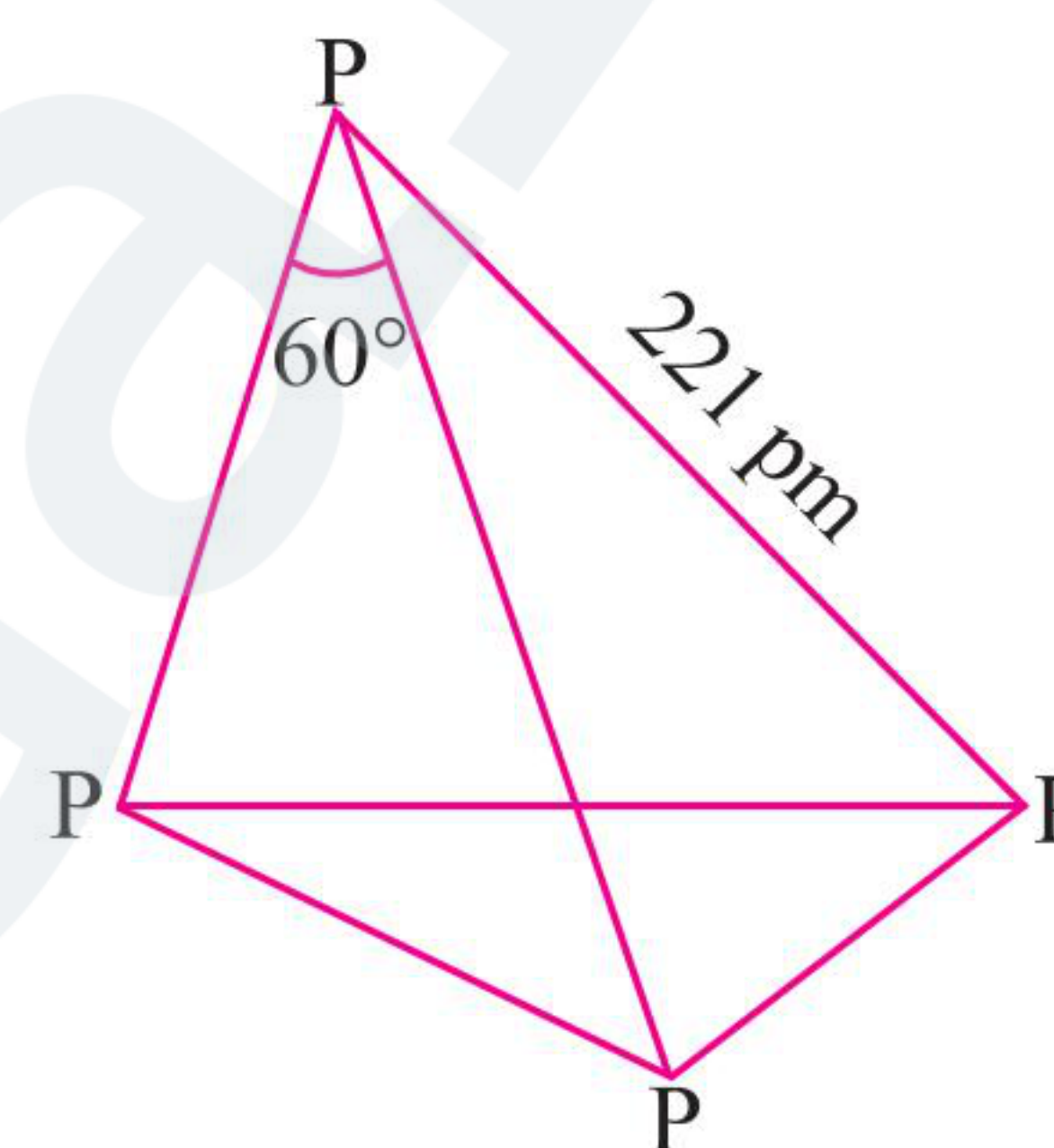


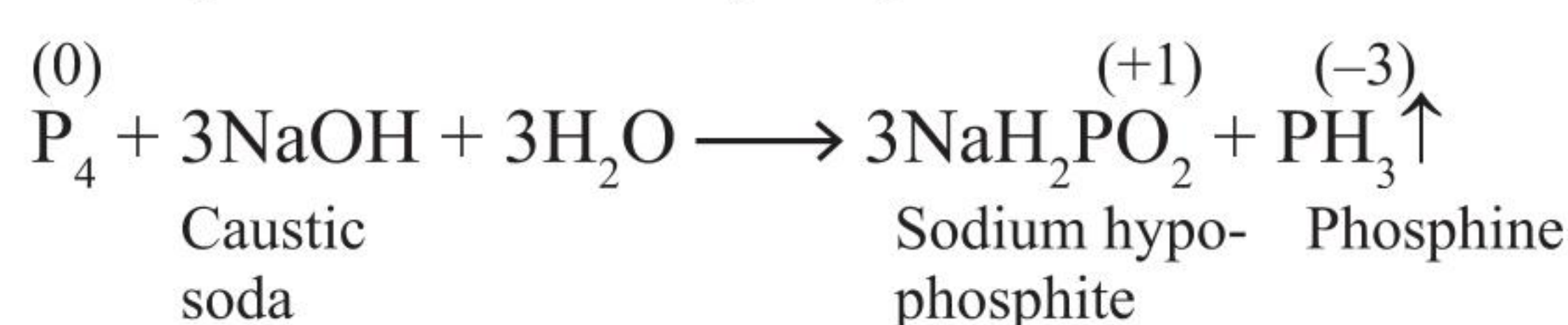
Fig. 2.5 Structure of white P_4

Property:

1. On exposure to light, white phosphorous turns yellow, hence it is also known as yellow phosphorous.
2. It is soft, translucent waxy solid with garlic odour. Being soft, it can be cut with a knife.
3. It is highly poisonous in nature. 0.15 g is the fatal dose. Persons working with phosphorous develop a disease in which the jaw bones decay and the disease is known as **phossy jaw**.
4. The various P_4 molecules are held together by weak van der Waals forces of attraction and hence the melting and boiling points of white phosphorous are quite low.
5. It is insoluble in water but readily dissolves in organic solvents such as CS_2 , alcohol and ether.
6. It contacts with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence**.
7. Its ignition temperature is low (about 30°C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therefore, kept under water.



8. It dissolves in caustic alkalis on boiling in an inert atmosphere and forms phosphine.



It is an example of disproportionation reaction.

9. It directly combines with halogens forming first, trihalides and then pentahalides.



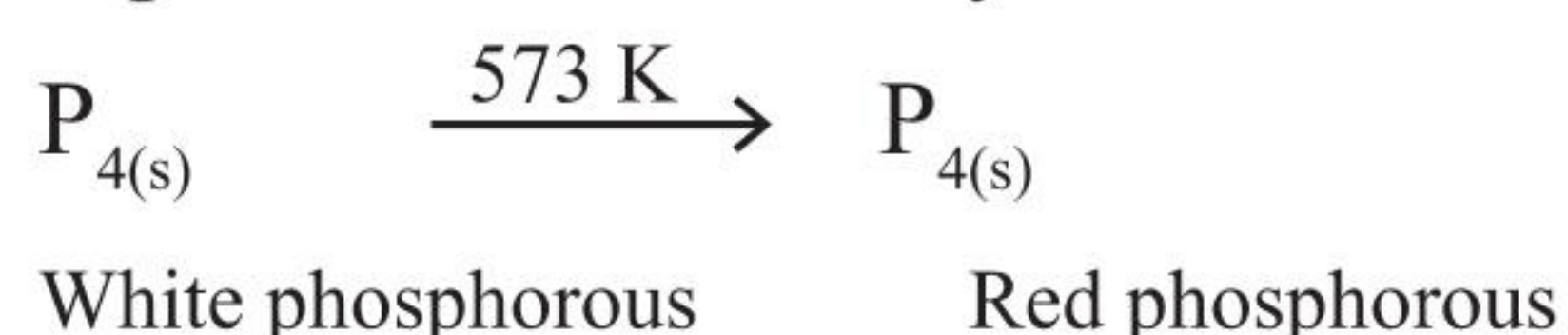
10. It combines with a number of metals forming phosphides.



11. It combines with sulphur with explosive violence forming a number of sulphides such as P_2S_3 , P_2S_5 , P_4S_3 and P_4S_7 .

2.11.1.2 Red Phosphorous

Preparation: It is obtained by heating white P_4 at 573 K in an inert atmosphere for several days.



Structure: Red phosphorous has polymeric structure, consisting of chains of P_4 tetrahedra linked together through covalent bonds (Fig. 2.6).

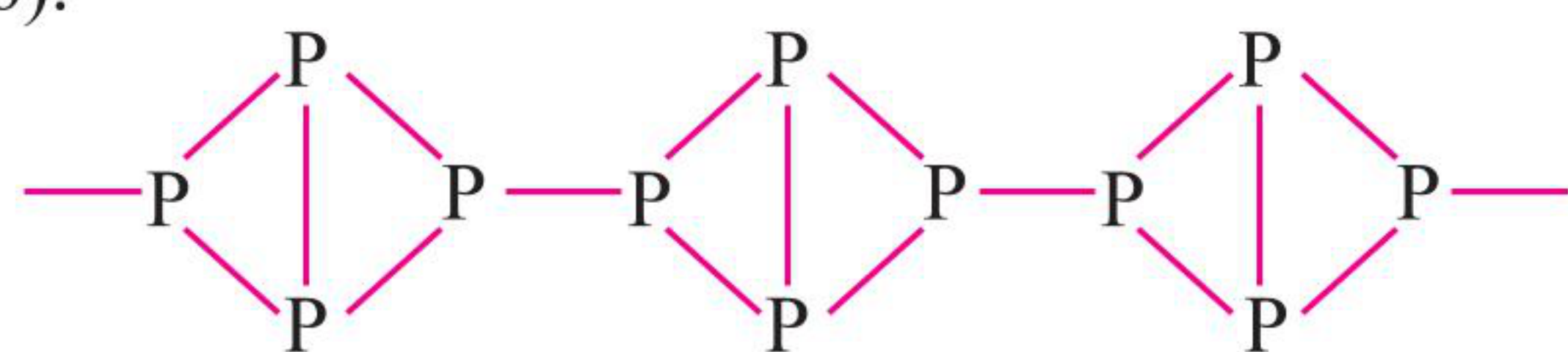
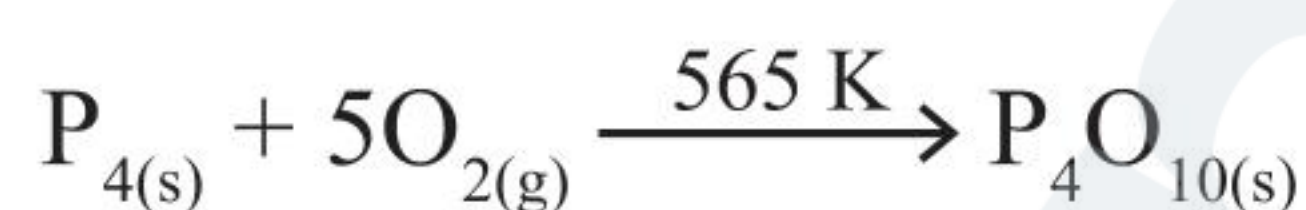


Fig. 2.6 Structure of red phosphorous

Property:

1. It is a hard crystalline odourless solid with iron grey lustre.
2. It is non-poisonous in nature.
3. It is insoluble in water as well in organic solvents such as CS_2 , alcohol and ether.
4. It is a relatively stable allotrope of phosphorus at room temperature. Its ignition temperature (543 K) is much higher than that of white phosphorus (303 K). Consequently, it does not catch fire easily.
5. It sublimes on heating giving vapours which are the same as given by white phosphorus. When these vapours are condensed, white phosphorus is obtained. Thus, red phosphorous is converted into white phosphorus.
6. It is denser (2.16 g cm^{-3}) than white phosphorous (1.84 g cm^{-3}) and is a bad conductor of electricity.
7. Being polymeric in nature, red phosphorous is less reactive than white phosphorus.
8. It burns in oxygen at 565 K to yield phosphorus pentoxide.



9. Being less reactive than white phosphorus, it reacts with halogens, sulphur and alkali metals only when heated forming their corresponding salts.

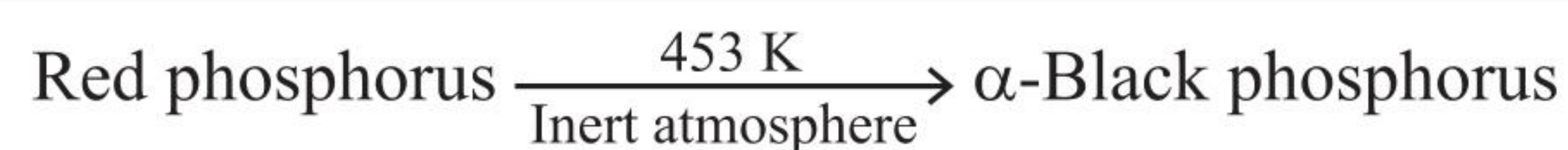


10. It does not react with caustic alkalis. This property is made use in separating, red phosphorus from white phosphorus.

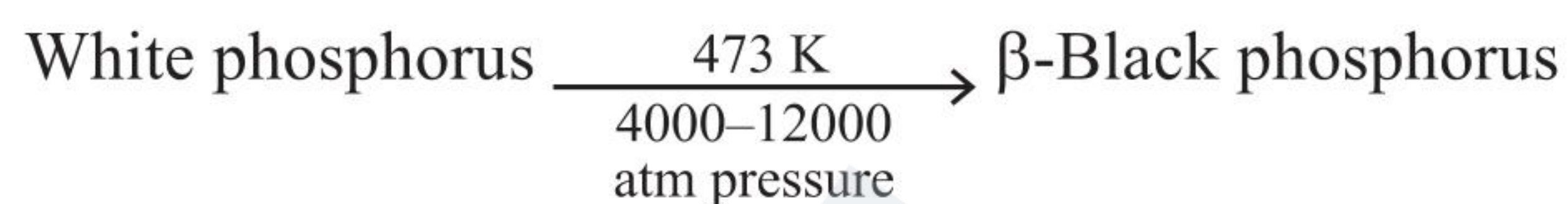
2.11.1.3 Black Phosphorous

It has two forms: α -black phosphorus and β -black phosphorus.

1. Preparation: α -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.



β -Black phosphorus (orthorhombic) is prepared by heating white phosphorus at 473 K under a very high pressure (4000–12000 atm.) in an inert atmosphere.



2. Structure: β -black phosphorus has a layered structure in which each phosphorus atom is covalently bonded to three neighbouring phosphorus atoms as shown in Fig. 2.7. The P—P—P angles are of 99° and P—P distance is 218 pm.

The adjacent layers are held 368 pm apart. The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives β -black phosphorus graphite like structure.

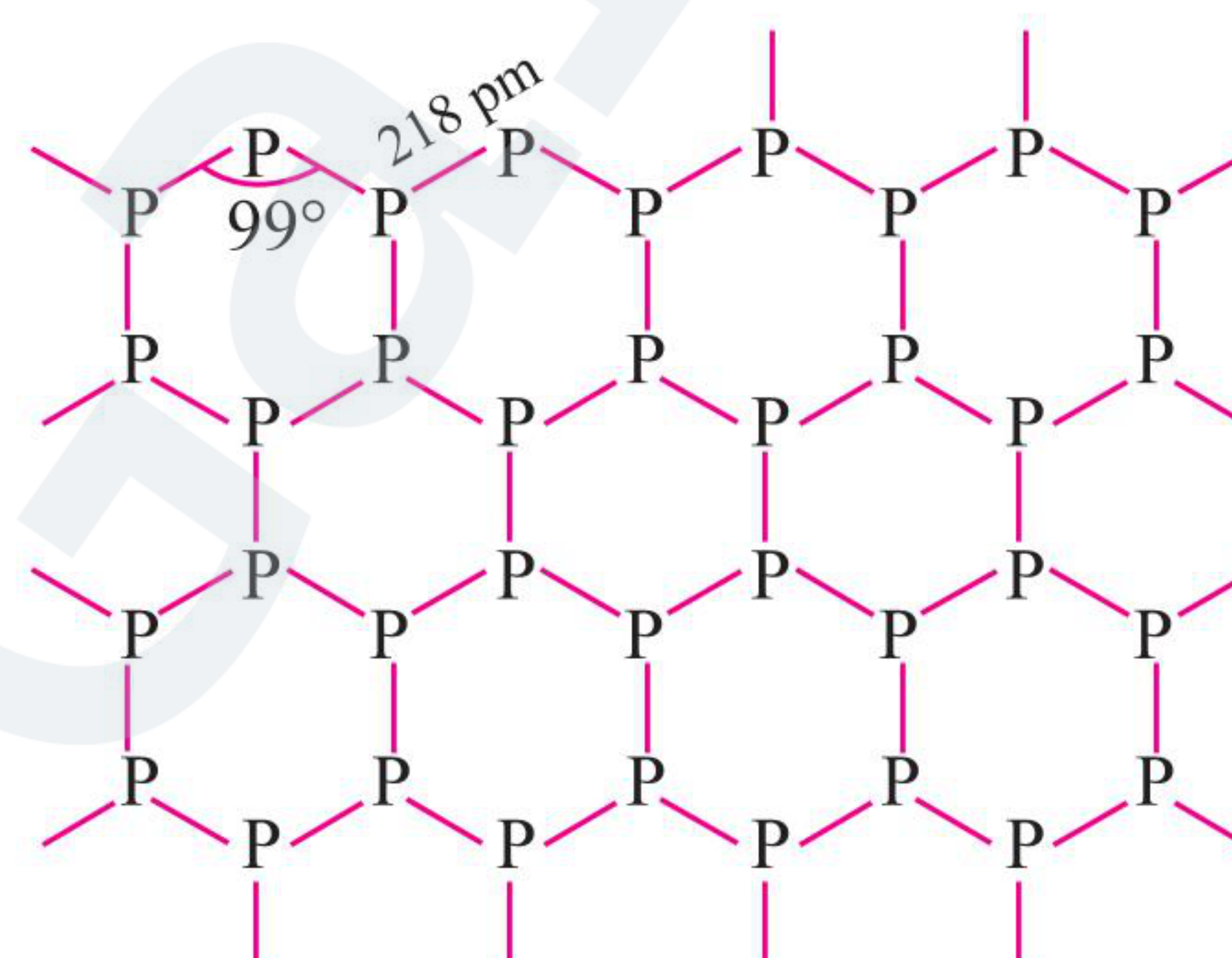


Fig. 2.7 Layered structure of β -black phosphorous

3. Properties:

- a. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.
- b. It is a very stable allotrope of phosphorous and does not oxidise in air until heated very strongly.
- c. It is good conductor of electricity.

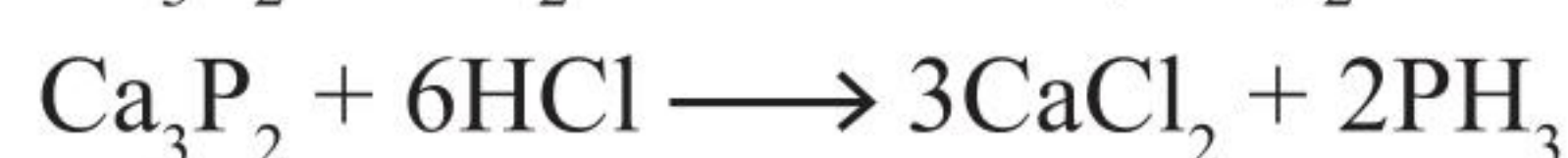
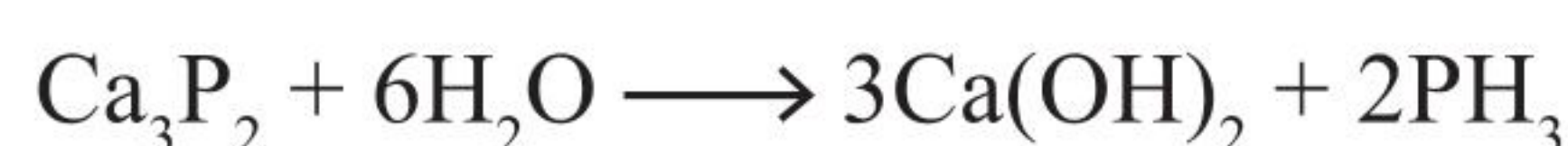
4. Uses:

- a. In the manufacture of food grade phosphates, detergent phosphates and pharmaceuticals.
- b. Elemental phosphorous is used in water industry.
- c. In the manufacture of organophosphorous compounds used as pesticides.
- d. In the form of phosphatic fertilisers in agriculture.

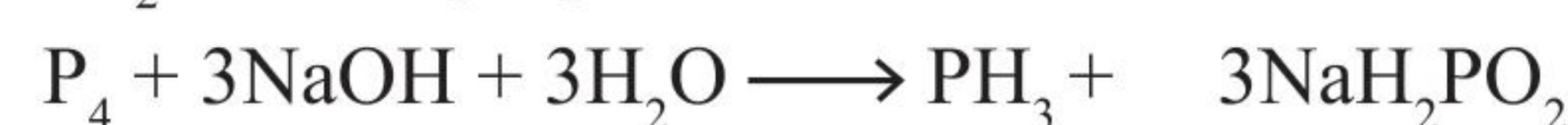
2.12 PHOSPHINE (PH_3)

Preparation:

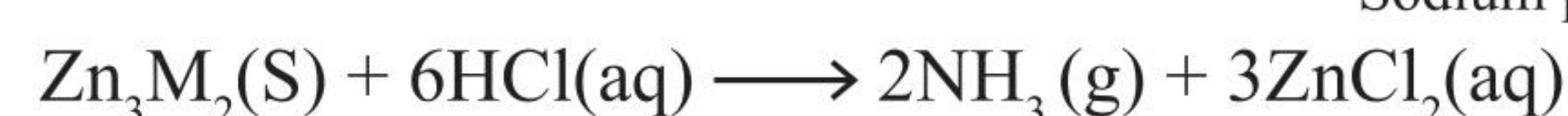
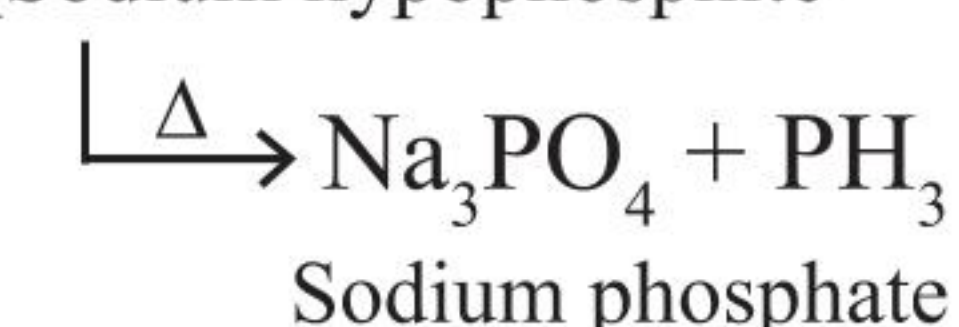
1. By hydrolysis of metal phosphides such as Ca_3P_2 or Na_3P with water or dilute HCl .



2. In laboratory, it is prepared by heating white phosphorous with concentrated NaOH solution in an inert atmosphere of CO_2 . It is disproportionation reaction.

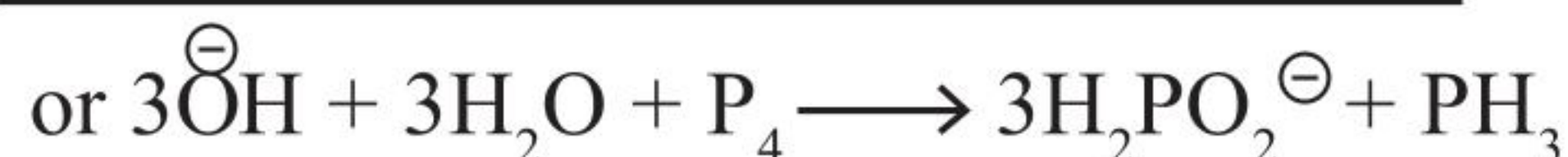
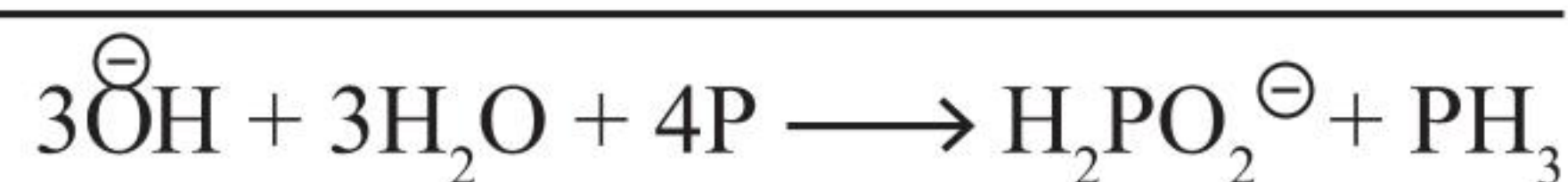


Phosphine (Sodium hypophosphite)



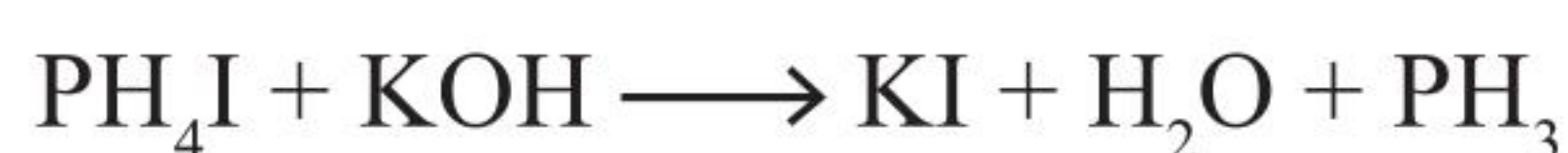
where $\text{M} = \text{As}, \text{Sb}$.

Ionic equation: It is disproportionation reaction in basic medium of P_4 to $H_2PO_2^\ominus$ (oxidation) and P_4 to PH_3 (reduction)

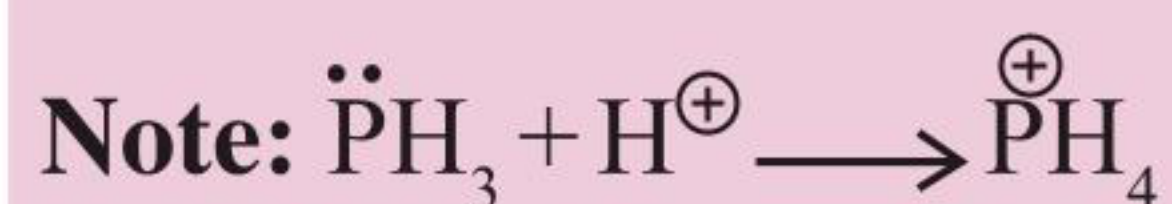
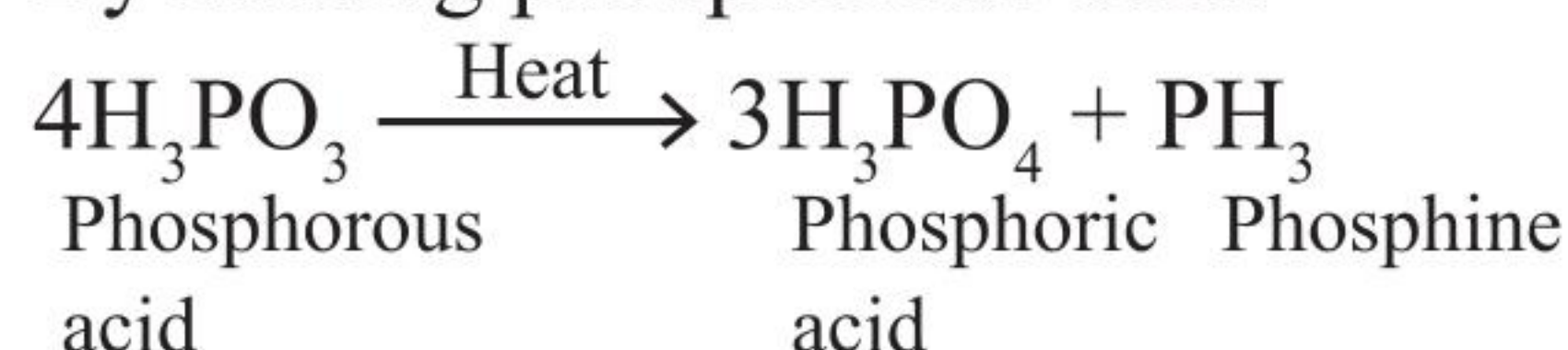


When pure, PH_3 is non-inflammable but becomes inflammable owing to the presence of P_2H_6 or P_4 vapours. This is the origin of flickering light called **will-o-the-wisp** which is sometimes seen in marshes. Therefore, a current of CO_2 is passed through the flask to displace air.

To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.



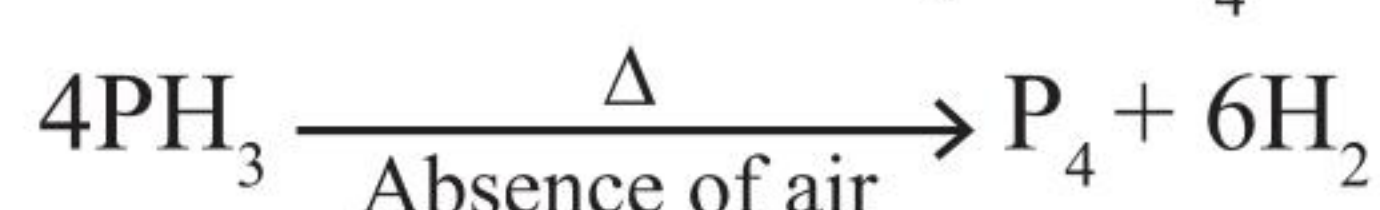
3. By heating phosphorous acid:



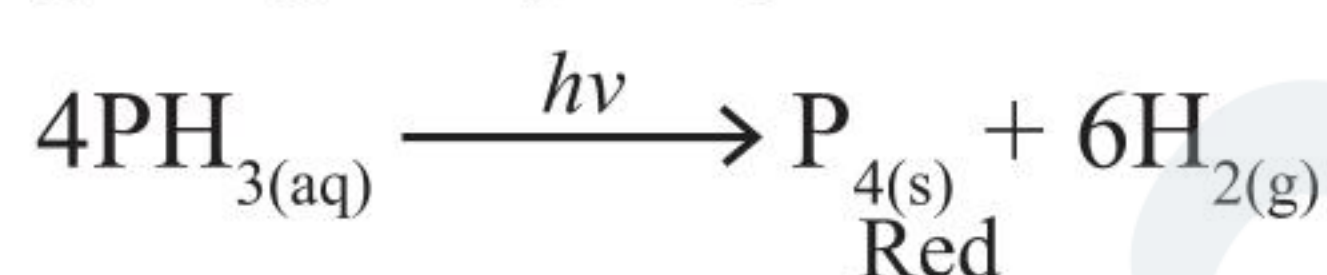
According to Drago's rule lp e^- 's on P lie in almost pure s-orbital, hence due to non-directional nature, its overlapping tendency is less in comparison to a lp e^- 's present in hybrid orbitals, which is direction as present $\ddot{N}H_3$.

Properties:

1. It is a colourless gas with rotten fish smell and is highly poisonous.
2. It is slightly soluble in water, the aqueous solution is neutral.
3. Phosphine decomposes on heating in absence of air into its constituent elements, i.e. P_4 and H_2 .



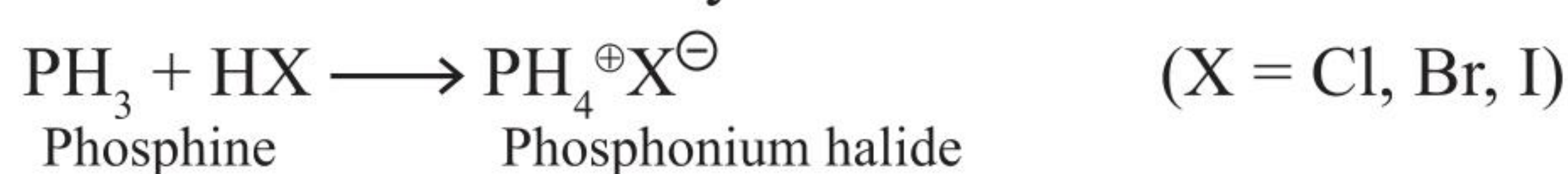
Solution of PH_3 in water decomposes in presence of light giving red phosphorous and H_2 .



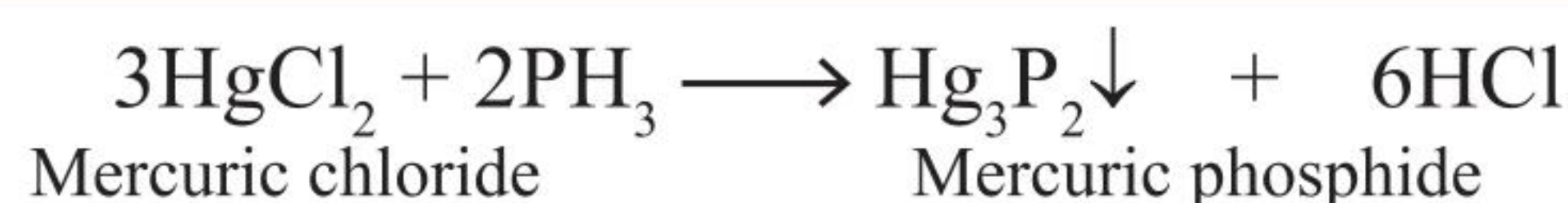
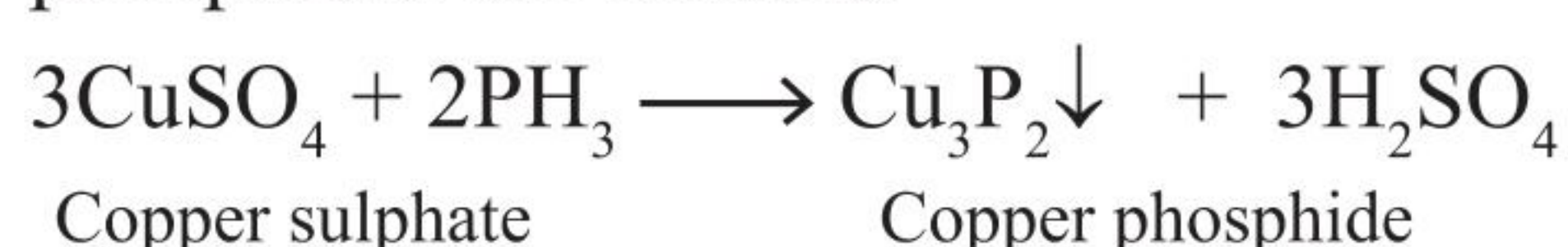
4. Phosphine explodes in contact with traces of oxidising agent like Cl_2 or Br_2 vapours, HNO_3 etc.



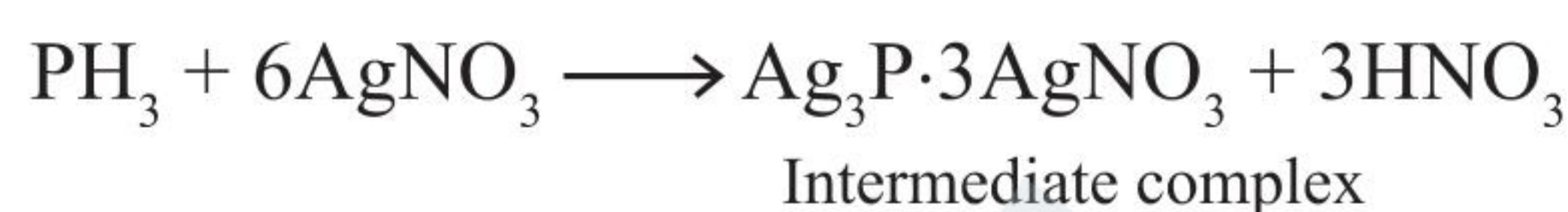
5. Phosphine is feebly basic and like NH_3 forms salts with mineral acids under anhydrous conditions.



6. When PH_3 is bubbled through the aqueous solutions of copper, and mercury salts, the precipitates of corresponding phosphides are formed.



7. With silver nitrate, first a complex of silver phosphide is produced, which is subsequently reduced in presence of water to metallic silver which appears as a black ppt.



Uses:

1. **Spontaneous combustion of PH_3 .** It is used as Holme's signals in deep seas and oceans for signalling danger points to steamers. Containers containing a mixture of calcium phosphide and calcium carbide are pierced and thrown into the sea. In contact with water, a mixture of phosphine and acetylene gases is produced. Phosphine frequently contains traces of highly inflammable diphosphine P_2H_6 which catches fire spontaneously. This ignites acetylene which burns with a luminous flame and thus serves as a signal to the approaching ship. **That is, PH_3 sometimes called cold fire.**
2. Shells containing calcium phosphide are exploded by warships. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of P_4O_{10} which act as smoke screens.

ILLUSTRATION 2.8

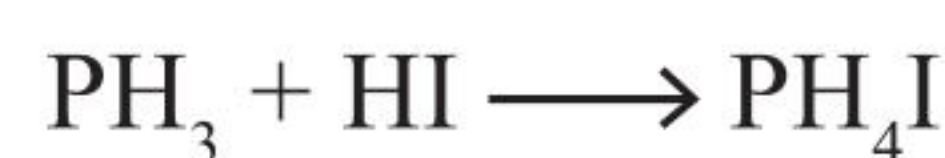
- a. Why does NO_2 dimerise?
- b. In what way can it be proved that PH_3 is basic in nature?

Sol.

- a. NO_2 contains odd number of valence electrons.

It behaves as an odd electron molecule hence it dimerises. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

- b. PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.

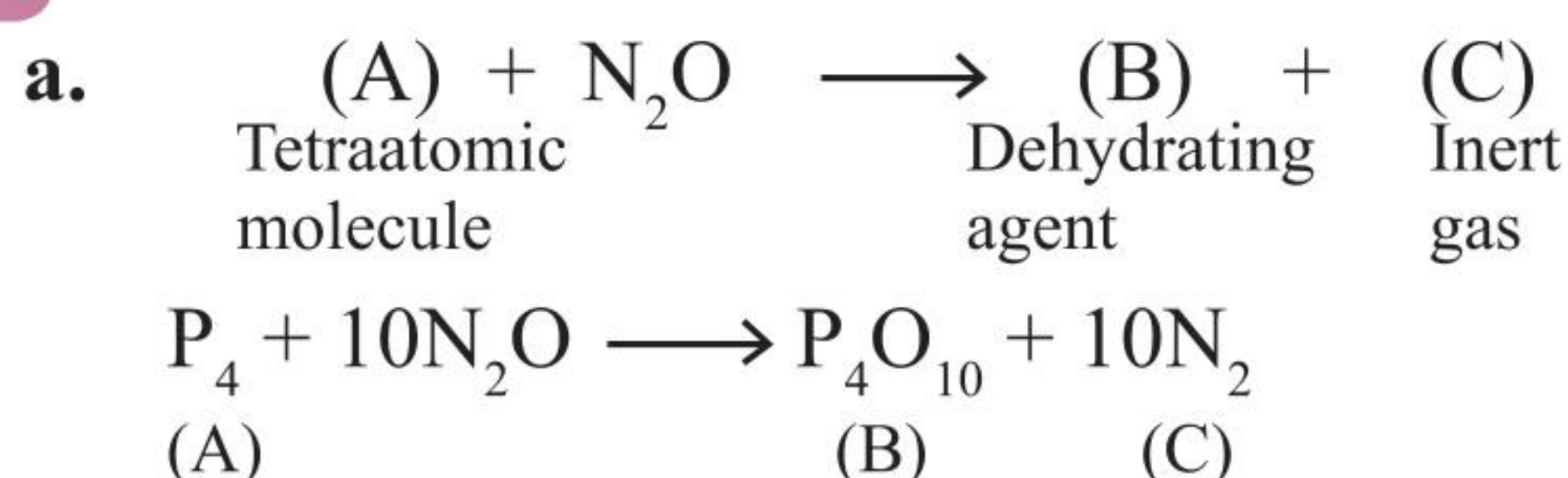


Due to lone pair of electrons on P in PH_3 , it acts as a Lewis base in the above reaction.

ILLUSTRATION 2.9

- a. A tetraatomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C). (B) is a dehydrating agent while substance (C) is a diatomic gas which shows almost inert behaviour. Identify (A), (B) and (C).
- b. Why red phosphorous is denser and chemically less reactive than white phosphorous?
- c. Why nitrous oxide supports combustion better than air?

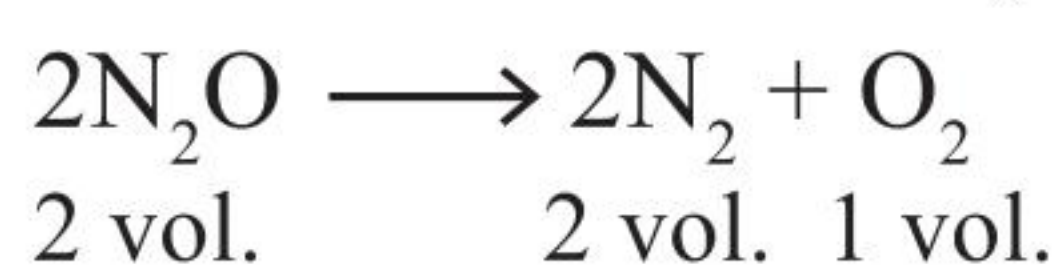
Sol.



(A) is tetratomic molecule, which on reaction with nitrogen (I) oxide, N_2O gives (B), i.e. P_4O_{10} which acts as a dehydrating agent, while (C) is N_2 , a diatomic gas which is inert.

b. Red phosphorous is regarded as a polymer consisting of chains of P_4 tetrahedra linked together. Hence red phosphorous is denser and less reactive than white phosphorous.

c. Air has $\sim 22\%$ O_2 in it, while N_2O on decomposition produces $\sim 33\%$ of O_2 by volume.



$$O_2 = \frac{\text{Total vol of } N_2 \text{ and } O_2}{3} \approx 33\%$$

Since $\%$ of O_2 produced by decomposition of N_2O is more, it acts as a better supporter of combustion.

ILLUSTRATION 2.10

- What is the role of phosphorous pentoxide in the preparation of N_2O_5 ?
- Phosphine is prepared in an inert atmosphere of CO_2 . Why?
- Red phosphorous is used for making matches. Why?

- Sol.**
- P_4O_{10} acts as strong dehydrating agent. It removes water molecules from nitric acid, HNO_3 to form N_2O_5 .

$$P_4O_{10} + 12HNO_3 \longrightarrow 4H_3PO_4 + 6N_2O_5$$
 - Phosphine, being inflammable, burns in air. It is therefore prepared in an inert atmosphere.
 - Red phosphorous is non-poisonous and has a high ignition point and hence red phosphorous is used for making matches.

ILLUSTRATION 2.11

- Nitric oxide turns brown in air. Why?
- Copper dissolves in HNO_3 but not in HCl . Why?

- Sol.**
- Nitric oxide directly reacts with oxygen of air and forms nitrogen dioxide, NO_2 which is brown in colour.

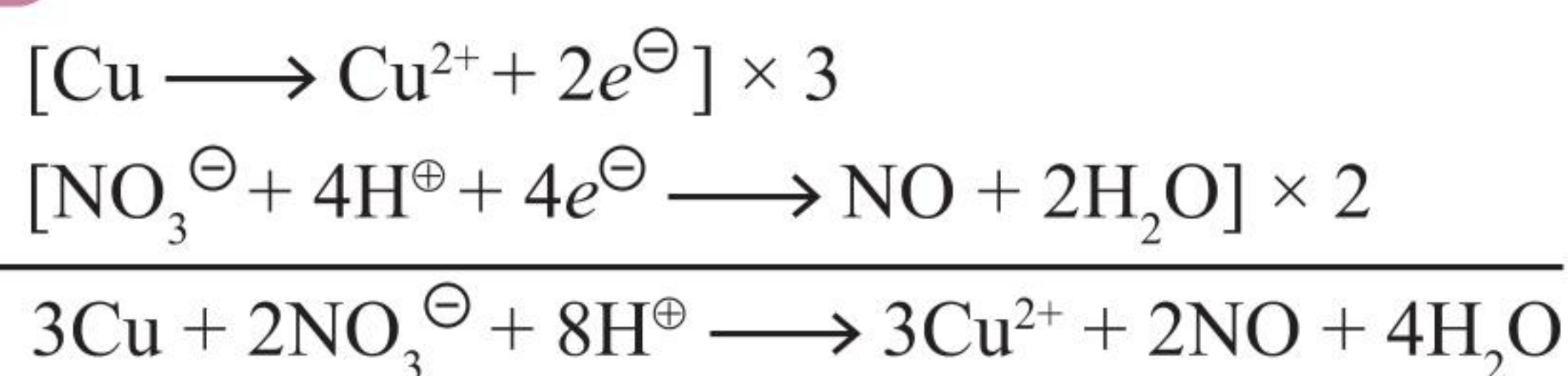
$$2NO + O_2 \longrightarrow 2NO_2$$

Colourless (air) Brown coloured gas
 - HNO_3 behaves as an oxidising agent and oxidises Cu to Cu^{2+} , which dissolves in HNO_3 as copper nitrate. On the other hand, HCl does not behave as an oxidising agent and hence copper does not dissolve in HCl .

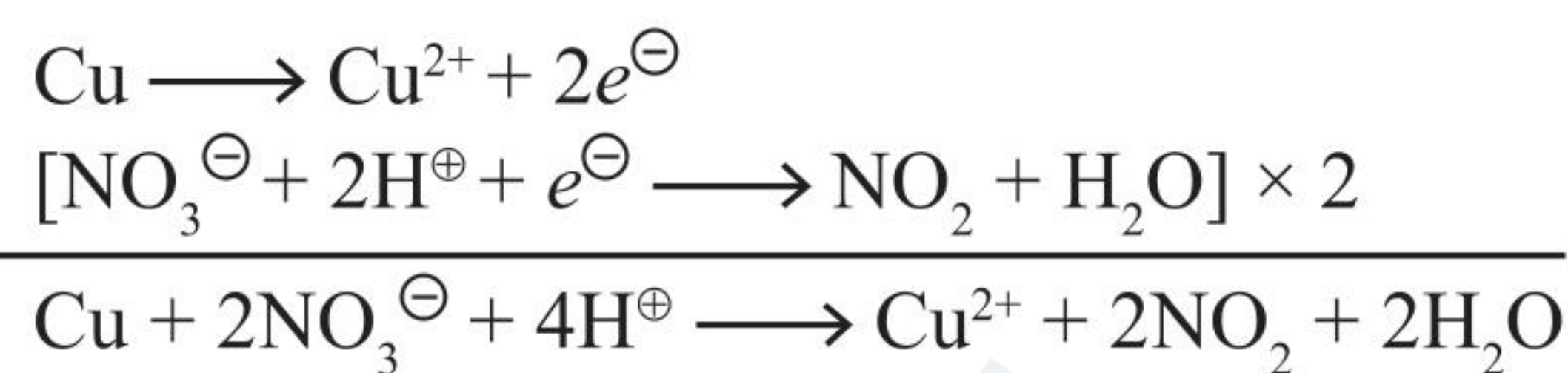
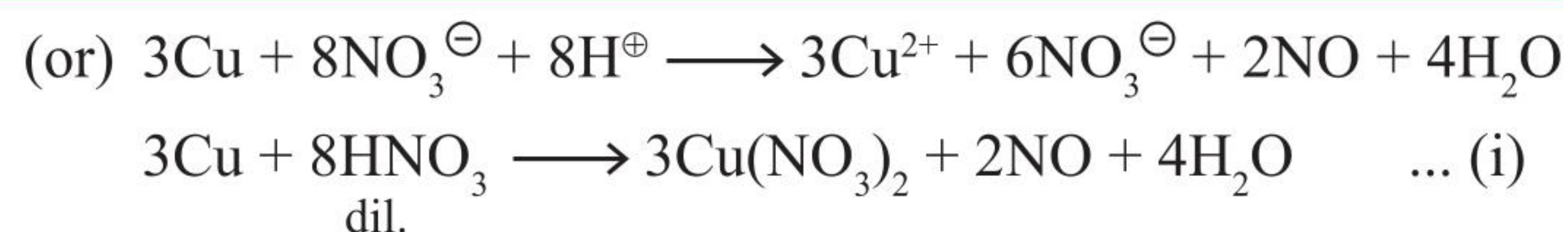
ILLUSTRATION 2.12

Calculate the number of moles of Cu and HNO_3 , when copper reacts with HNO_3 to give NO and NO_2 in the (2 : 1) molar ratio.

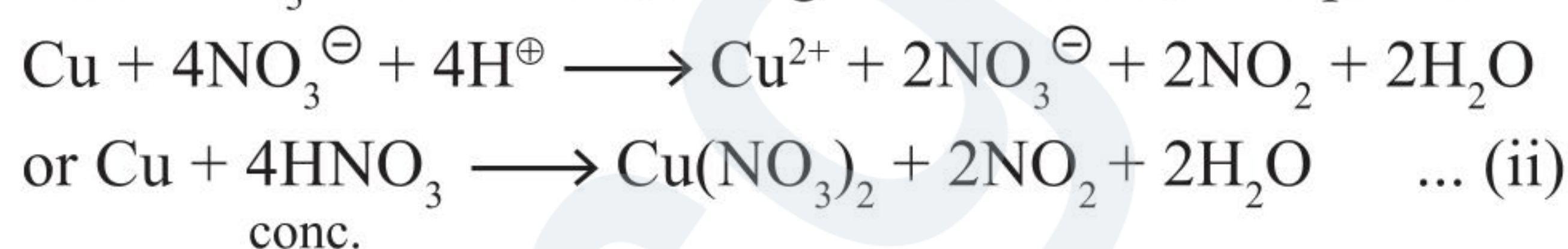
Sol.



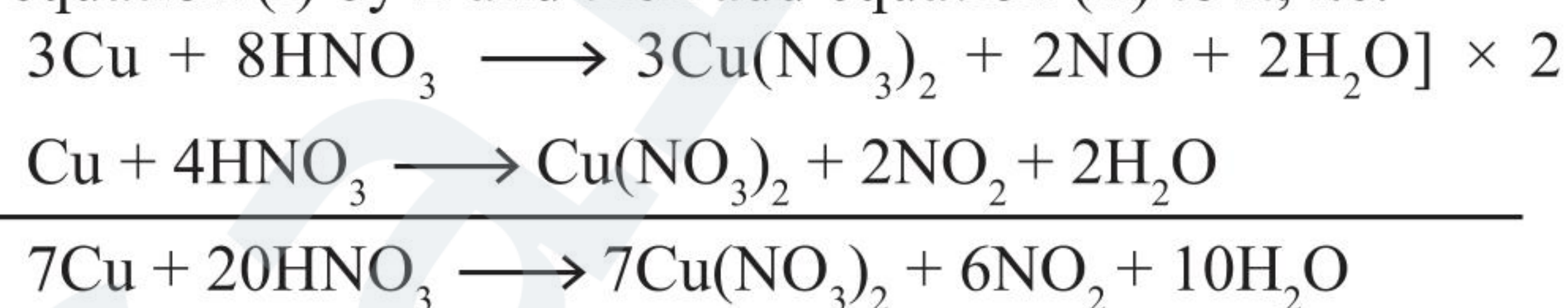
Add $6NO_3^-$ to both sides to get the molecular equation.



Add $2NO_3^-$ to both sides to get the molecular equation.



To get NO and NO_2 in the molar ratio (2 : 1), multiply equation (i) by 2 and then add equation (ii) to it, i.e.



Ans: Moles of $Cu = 7$, moles of $HNO_3 = 20$

2.13 PHOSPHOROUS HALIDES

Phosphorous forms two types of halides:

- Trihalides, PX_3 ; where $X = F, Cl, Br$ and I .
- Pentahalides, PX_5 ; where $X = F, Cl, Br$.

2.13.1 PHOSPHOROUS TRICHLORIDE (PCl_3)

Preparation:

- By passing dry Cl_2 over heated white phosphorous

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
- By the action of thionyl chloride on white phosphorous

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

3. Properties:

- It is a colourless, pungent smelling oily liquid, which boils at 347 K and solidifies at 161 K.
- It fumes in moist air as PCl_3 hydrolysis in moist air resulting in the formation of HCl .

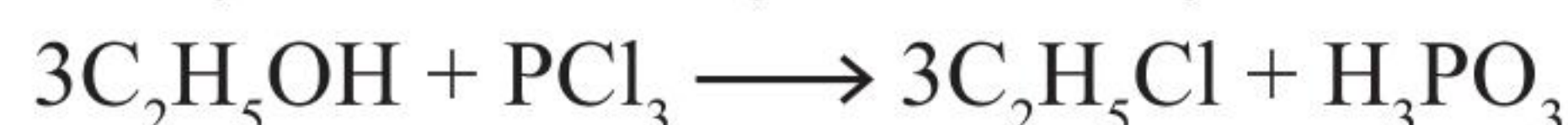


- Reaction with conc. H_2SO_4

$$H_2SO_4 + PCl_3 \longrightarrow SO_2Cl_2 + SO_2 + HPO_3 + 2HCl$$

Sulphuric acid Sulphuryl chloride
- PCl_3 acts as reducing agent

$$PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$$
- It reacts with organic compounds containing $-OH$ group, where $-OH$ group is replaced by $-Cl$ group, e.g.



That is why PCl_3 is widely used in organic chemistry to convert carboxylic acids to acid chlorides and alcohols to alkyl halides.

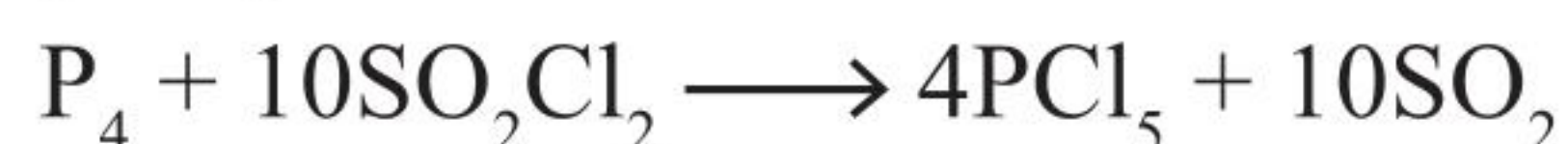
2.13.2 PHOSPHOROUS PENTACHLORIDE (PCl_5)

Preparation:

- By the reaction of white phosphorous with excess of dry Cl_2 .

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

2. By the action of sulphuryl chloride, SO_2Cl_2 on white phosphorous.



3. **Structure:** P in PCl_5 undergoes sp^3d hybridisation and PCl_5 has trigonal bipyramidal geometry in gaseous and liquid state (Fig. 2.8).

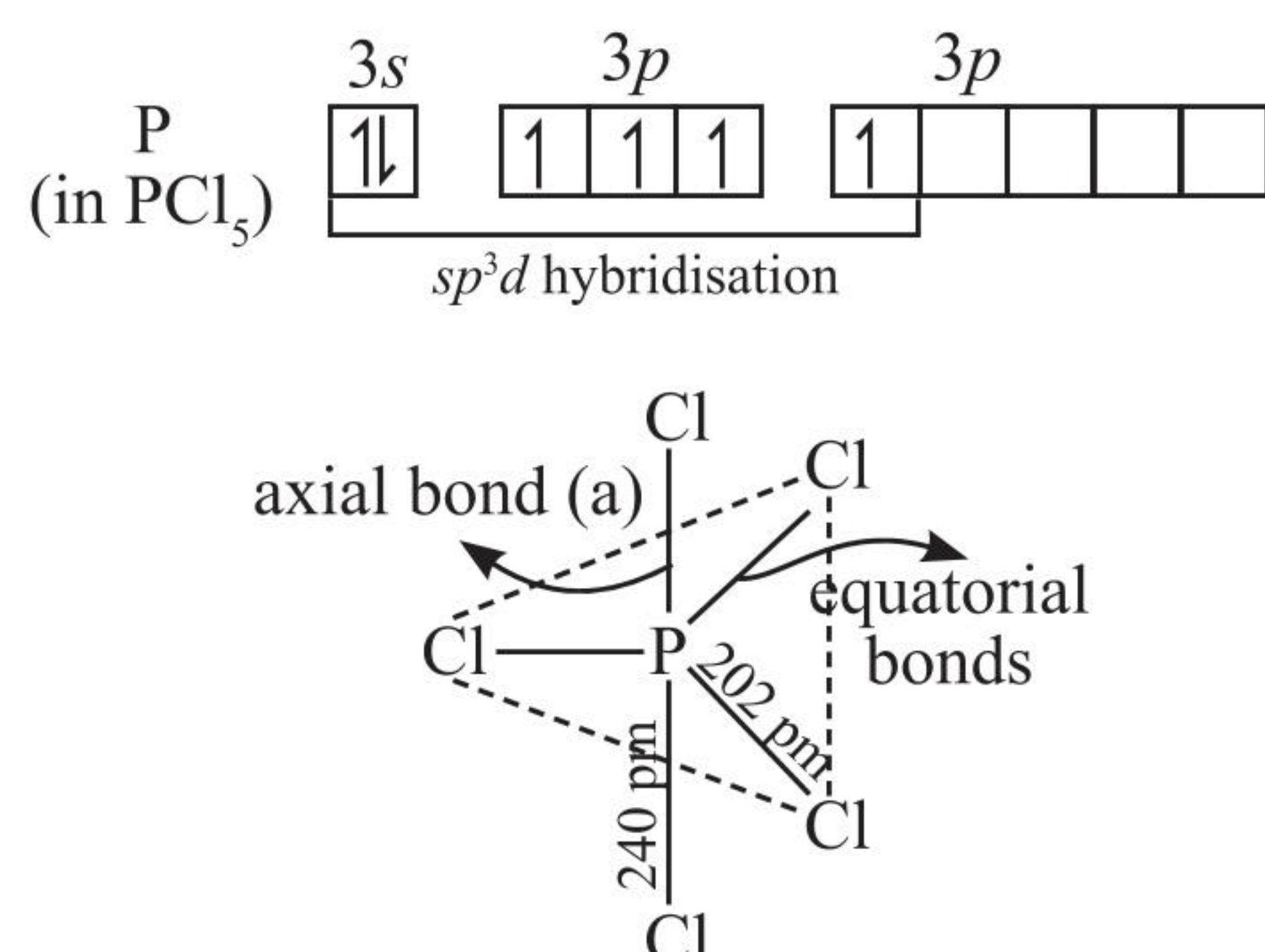


Fig. 2.8 Structure of PCl_5

The three equatorial P—Cl bonds are equivalent, while the two axial P—Cl bonds are equivalent and larger than equatorial bonds. $\angle\text{ClPCl}$ in equatorial plane is 120° , and in axial plane is 90° .

In the **solid state**, PCl_5 exists as an ionic solid

$[\text{PCl}_4]^+ [\text{PCl}_6]^-$ in which $[\text{PCl}_4]^+$ is tetrahedral while $[\text{PCl}_6]^-$ is octahedral. (Fig. 2.9(a) and (b))

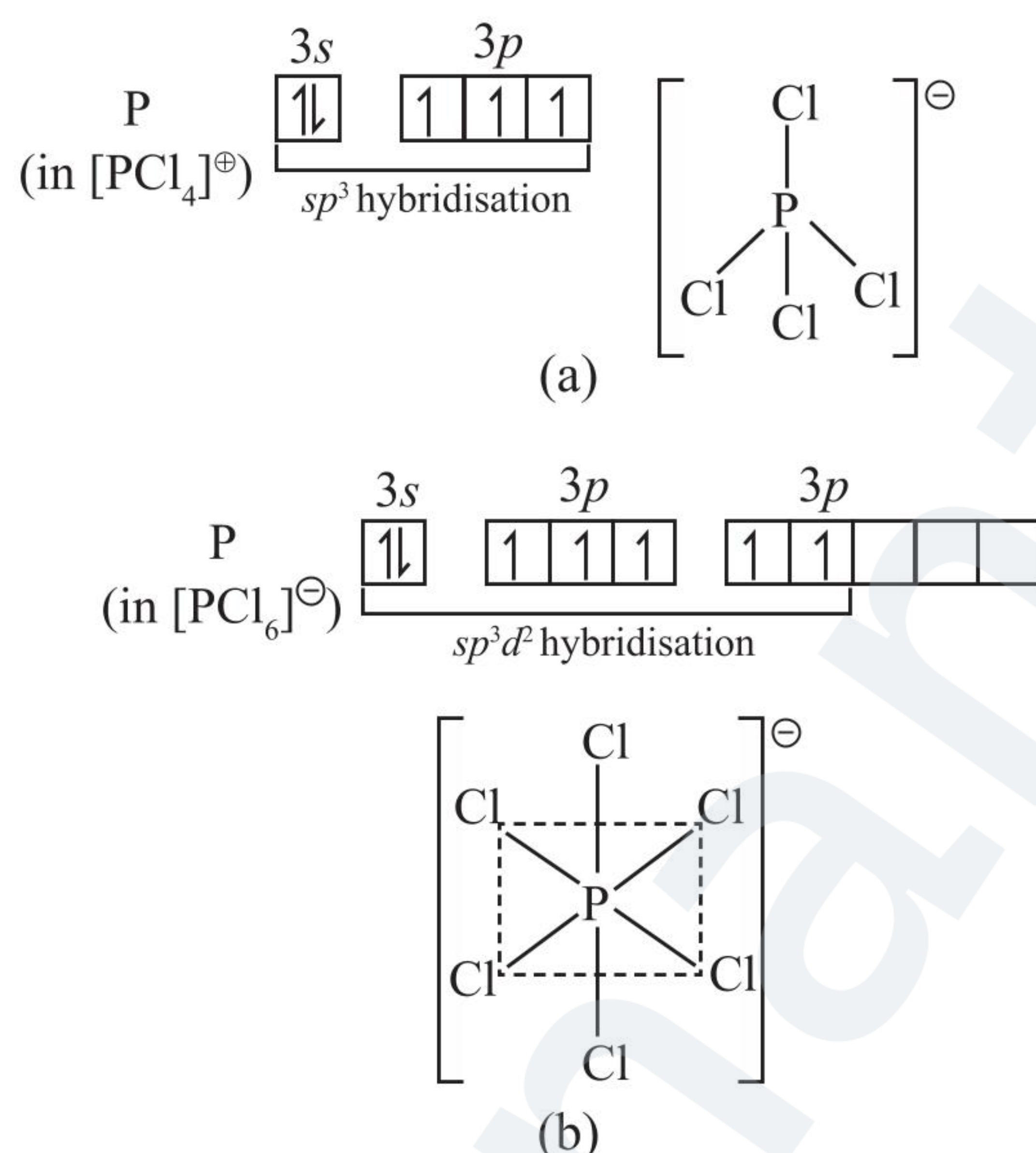
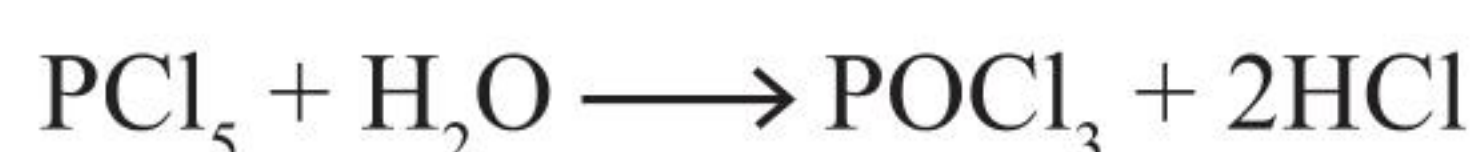


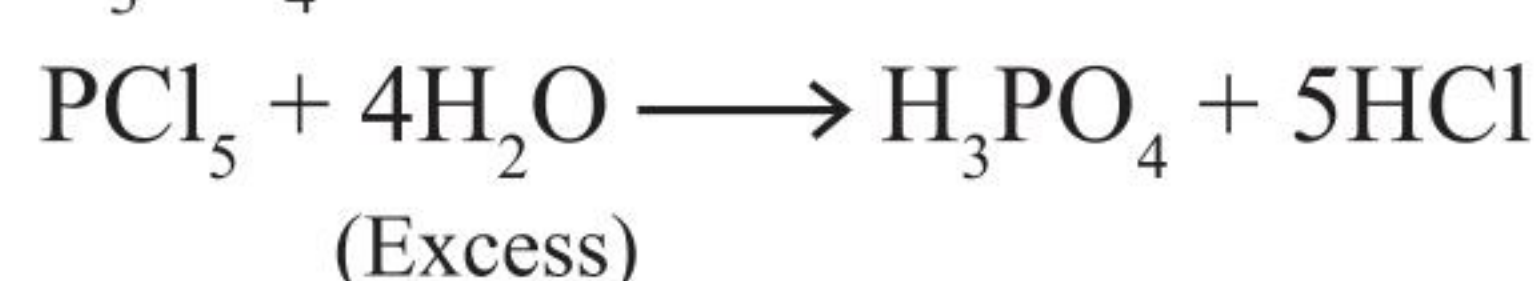
Fig. 2.9 (a) Structure of $[\text{PCl}_4]^+$ and (b) Structure of $[\text{PCl}_6]^-$

4. Properties:

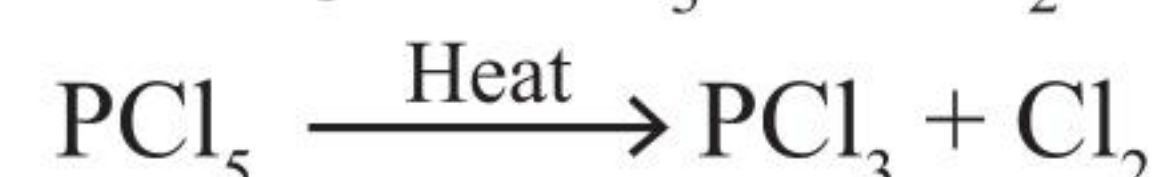
- PCl_5 is a yellowish white crystalline solid with a characteristic smell.
- In moist air, it hydrolyses to POCl_3 and finally gets converted to phosphoric acid.



With excess of water, PCl_5 reacts violently to produce H_3PO_4 and HCl .



- On heating, it sublimes but decomposes on stronger heating to PCl_3 and Cl_2 .



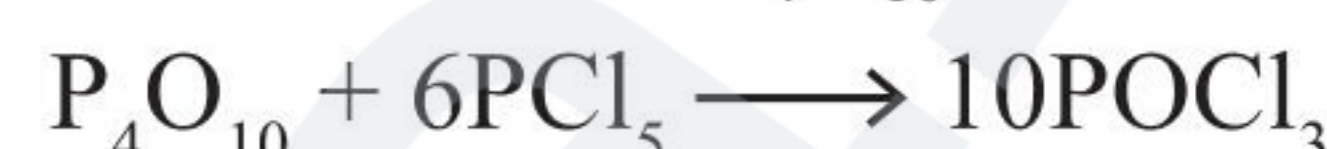
- PCl_5 converts carboxylic acids to acid chlorides and alcohols to alkyl halides, i.e. it is used in organic synthesis.



- PCl_5 reacts with finally divided metal on heating to give corresponding chlorides.



- Reaction with P_4O_{10} .



- Reaction with SO_2 .

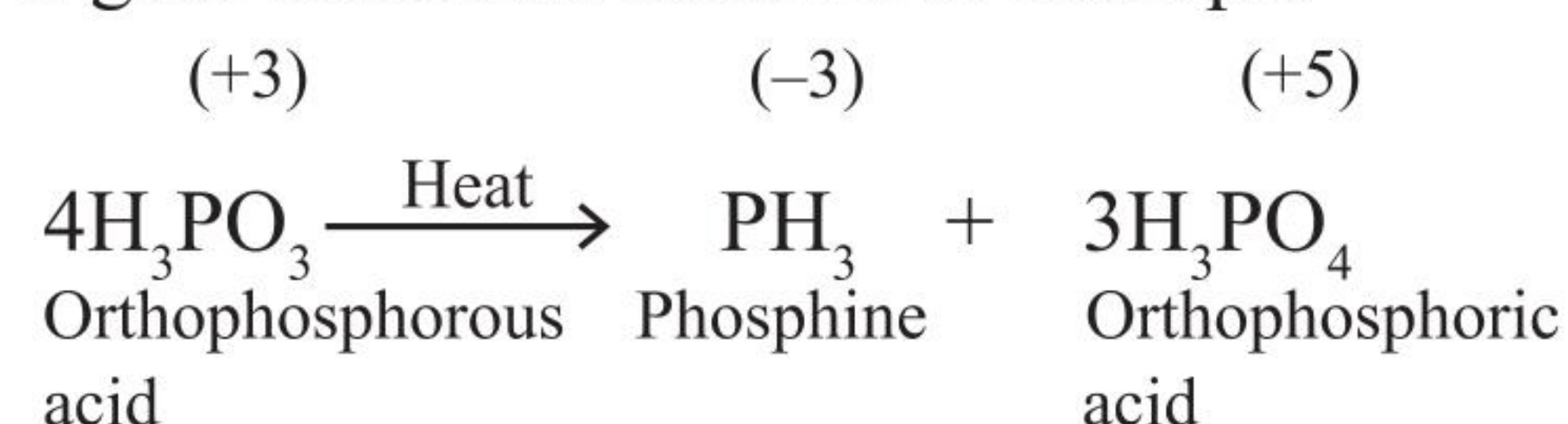


2.14 OXOACIDS OF PHOSPHOROUS

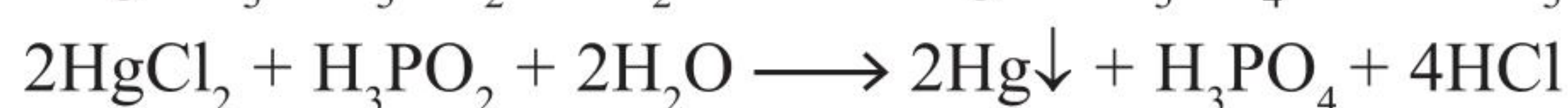
- The oxoacids of nitrogen have no phosphorous analogues and although HPO_3 has the same empirical formula as HNO_3 , it is a polymeric compound unlike HNO_3 . The difference lies in the fact that strong $p\pi-p\pi$ bonding does not occur between phosphorous and oxygen. However, in all the oxyacids of phosphorous and their salts, the terminal P—O bonds are shorter than expected value for a P—O single bond, from which it is assumed that σ bonding between P and O is augmented by $(p\pi-d\pi)$ bonding between empty 3d orbitals on P and filled 2p orbital on oxygen to give P—O linkages multiple bond character.

The phosphorous oxoacids can be divided into two classes:

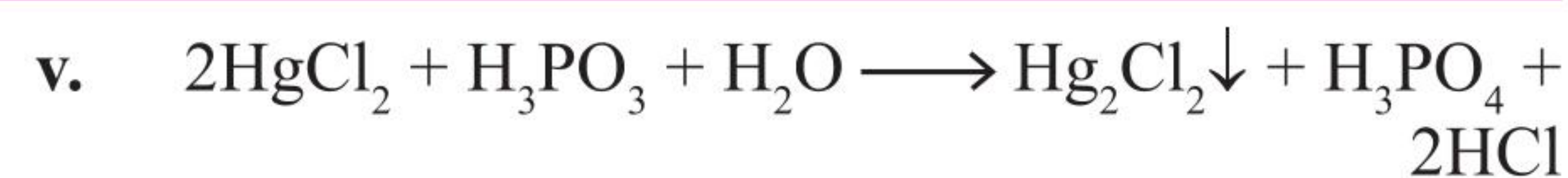
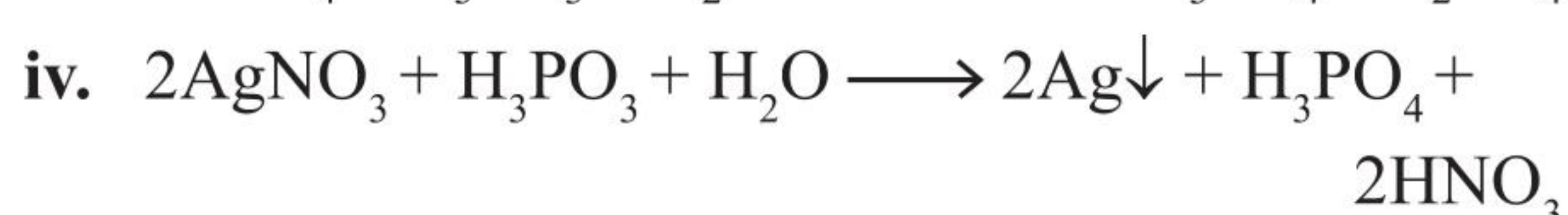
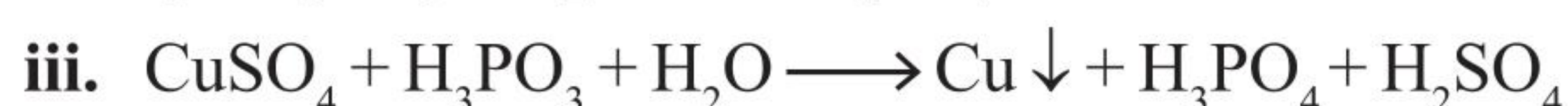
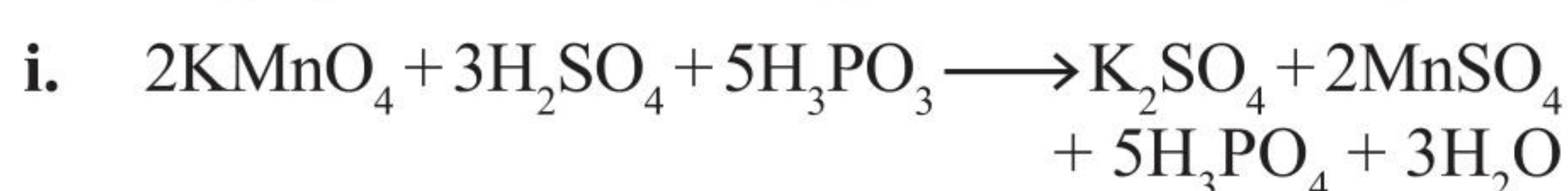
- Phosphorous acids, in which the formal oxidation state of P is +1 and +3.
 - Phosphoric acids, in which the formal oxidation state of P is +5.
- Few important points about oxoacids of phosphorous are as follows:
 - In all oxoacids, phosphorous is tetrahedrally surrounded by four other atoms or groups.
 - All these acids contain at least one P = O and one P—OH bond.
 - The oxoacids in which phosphorus has oxidation state less than +5, contain, in addition to P = O and P—OH bonds, either P—H (e.g., H_3PO_2 , H_3PO_3) or P—P (e.g., $\text{H}_4\text{P}_2\text{O}_6$) bonds but not both.
 - The oxoacids in +3 oxidation state undergo disproportionation reaction to give compounds in lower and higher oxidation states. For example



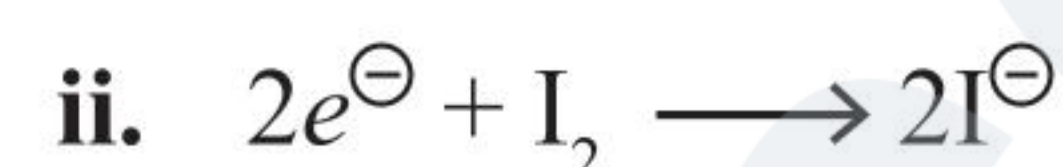
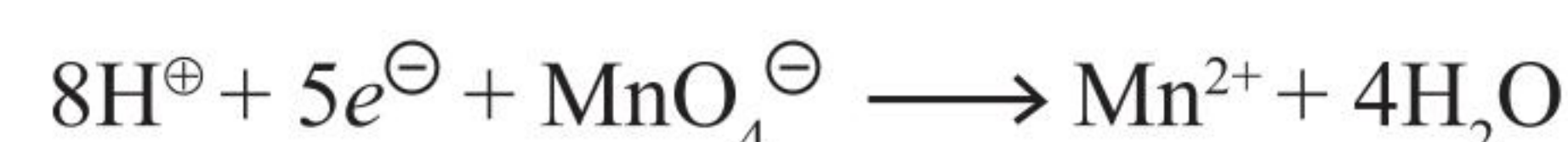
- e. Acids which contain P—H bonds have behave as reducing agents. For example, hypophosphorous acid (H_3PO_2) is a good reducing agent as it contains two P—H bonds and thus reduces AgNO_3 to metallic silver and HgCl_2 to Hg.



H_3PO_3 also acts as a reducing agent though weaker than H_3PO_2 because it contains only one P—H bond as compared to two in H_3PO_2 . It reduces acidified KMnO_4 , I_2 , and salts of copper, silver, mercury, etc.



Ionic equations:



Similarly, the ionic equation for reaction (iii), (iv) and (v) can be written.

- f. Oxoacids of phosphorous are summarised in Table 2.5.

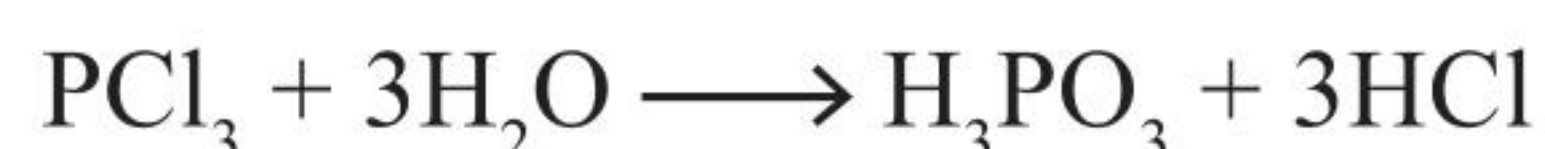
Table 2.5 Some oxoacids of phosphorous

	Name	Formula and O.S.	Characteristics bonds and their number	Basicity	Methods of preparation
1.	Orthophosphoric acid	H_3PO_4 (+5)	Three P—OH, one P=O	Tribasic	$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O}$ (Excess) $\longrightarrow 4\text{H}_3\text{PO}_4$
2.	Permonooxophosphoric acid	H_3PO_5 (+5)	Two P—OH, one P=O, one P—O—O—H	Tribasic	$\text{P}_4\text{O}_{10} + 4\text{H}_2\text{O}_2$ (30%) + $2\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_5$
3.	Orthophosphorous acid (Phosphonic acid)	H_3PO_3 (+3)	Two P—OH, one P—H, one P=O	Dibasic	$\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_3$ $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
4.	Hypophosphorous acid (Phosphinic acid)	H_3PO_2 (+1)	One P—OH, two P—H, one P=O	Monobasic	$2\text{P}_4 + 3\text{Ba}(\text{OH})_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{PH}_3 + 3\text{Ba}(\text{H}_2\text{PO}_2)_2$ $\text{Ba}(\text{H}_2\text{PO}_2)_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{H}_3\text{PO}_2$ $\text{P}_4 + 3\text{NaOH} \longrightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3 + 3\text{H}_2\text{O}$
5.	Metaphosphoric acid (exists in polymeric form), e.g.,	HPO_3 (+5)	One P—OH, two P=O	Monobasic	$2\text{H}_3\text{PO}_4 \xrightarrow{520\text{ K}} \text{H}_4\text{P}_2\text{O}_7 \xrightarrow{870\text{ K}} 2\text{HPO}_3$
	Cyclotrimetaphosphoric acid	$(\text{HPO}_3)_3$ (+5)	Three P—OH, three P=O, three P—O—P	Tribasic	$3\text{H}_3\text{PO}_3 + 3\text{Br}_2 \xrightarrow[\text{Sealed tube}]{\Delta} (\text{HPO}_3)_3 + 6\text{HBr}$
	Linear polymetaphosphoric acid	$(\text{HPO}_3)_n$ (+5)	$n(\text{P}=\text{O})$, $n(\text{P}—\text{OH})$, $n(\text{P}—\text{O}—\text{P})$	Polybasic	$n\text{H}_3\text{PO}_4 \xrightarrow[316^\circ\text{C}]{\text{Heat}} (\text{HPO}_3)_n + n\text{H}_2\text{O}$
6.	Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$ (+5)	Four O—H, two P=O, one P—O—P	Tetrabasic	$2\text{H}_3\text{PO}_4 \xrightarrow{523\text{ K}} \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$
7.	Peroxodiphosphoric acid	$\text{H}_4\text{P}_2\text{O}_8$ (+5)	Four O—H, two P=O, one P—O—O—P	Tetrabasic	Electrolysis of a mixture of $\text{K}_2\text{HPO}_4 + \text{KF}$
8.	Pyrophosphorous acid	$\text{H}_4\text{P}_2\text{O}_5$ (+3)	Two P—OH, two P—H, two P=O, one P—O—P	Dibasic	$5\text{H}_3\text{PO}_3 + \text{PCl}_3 \longrightarrow 3\text{H}_4\text{P}_2\text{O}_5 + 3\text{HCl}$
9.	Hypophosphoric acid	$\text{H}_4\text{P}_2\text{O}_6$ (+4)	Four P—OH, two P=O, one P—P	Tetrabasic	$2\text{P}(\text{red}) + 4\text{NaOCl} + 2\text{H}_2\text{O} \longrightarrow \text{H}_4\text{P}_2\text{O}_6 + 4\text{NaCl}$

ILLUSTRATION 2.13

- Why does PCl_3 fume in moisture?
- Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.
- How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?
- Give the disproportionation reaction of H_3PO_3 .

Sol. a. PCl_3 hydrolyses in the presence of moisture and gives fumes of HCl .

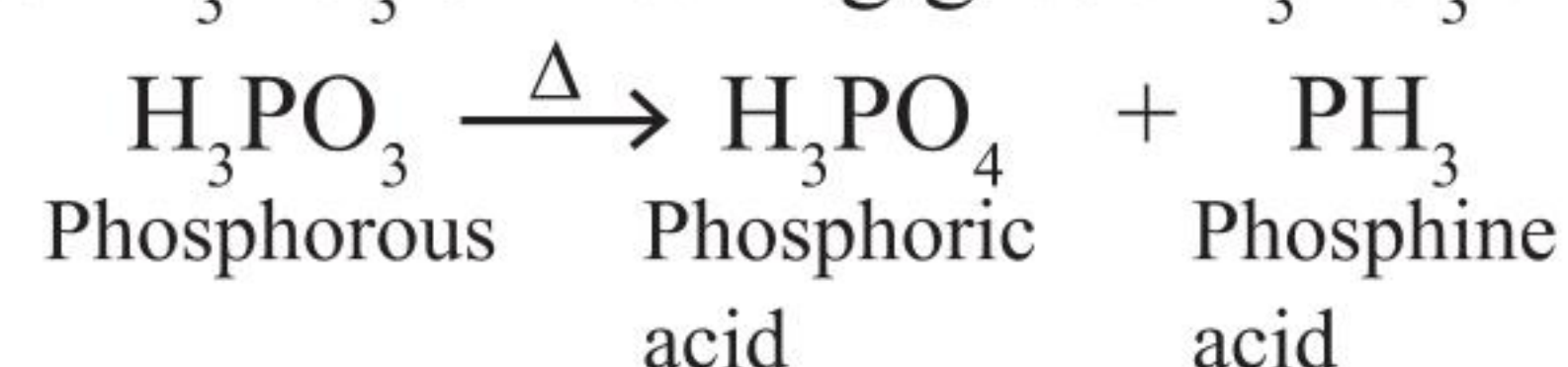


- b. All 5 bonds are not equivalent.

PCl_5 has trigonal bipyramidal geometry, the three P–Cl bonds in the equatorial plane have same bond length and two P–Cl bonds in the axial plane have same bond length. Axial P–Cl bonds are longer than equatorial P–Cl bonds.

- c. In H_3PO_2 , two H atoms are bonded directly to P atom, hence due to weak P–H bonds H_3PO_2 acts as a reducing agent.

- d. H_3PO_3 on heating gives H_3PO_4 and PH_3 .



CONCEPT APPLICATION EXERCISE 2.1

Subjective Type

- Write complete balanced reactions for the following:
 - Red phosphorous reacts with iodine in presence of water.
 - White phosphorous is boiled with a strong solution of NaOH in an inert atmosphere.
 - Phosphorous reacts with conc. HNO_3 to give H_3PO_4 .
 - Iodine reacts with concentrated nitric acid.
 - Orthophosphoric acid is heated with nitric acid and ammonium molybdate.
 - Disodium hydrogen phosphate is added to ammonical solution of magnesium sulphate.
 - Magnesium is burnt in air and the product is treated with water.
 - Phosphine is passed through AgNO_3 solution.
 - A mixture of air and ammonia is passed over heated platinum gauze.
 - Gold is treated with aqua regia.
 - Water is added to calcium phosphide.
 - Calcium phosphate is heated with a mixture of sand and carbon.

- Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
- Zinc is treated with very dilute nitric acid.
- Phosphine is treated with an acidified CuSO_4 solution.

2. Describe the action of heat on the following compounds:

- Ammonium nitrate
- Ammonium nitrite
- Ammonium chloride
- Ammonium dichromate
- Orthophosphoric acid
- Phosphorous acid
- Hypophosphorous acid
- Copper nitrate

3. Complete and balance the following reactions:

- $\text{P}_4\text{O}_{10} + \text{PCl}_5 \longrightarrow$ _____
- $\text{NH}_3 + \text{NaOCl} \longrightarrow$ _____ + $\text{NaCl} + \text{H}_2\text{O}$
- $\text{Ca}(\text{PO}_4)_3 + 4\text{H}_3\text{PO}_4 \longrightarrow$ _____
- $\text{AgCl} + \text{NH}_4\text{OH} \longrightarrow$ _____ + _____
- $\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{PbO} +$ _____ + _____
- $\text{Mg} + \text{HNO}_3 \longrightarrow$ _____ + _____

- In hyponitrous acid, If X is number of σ bonds, Y is the number of non-bonding electrons and Z is the number of π bonds. Then value of $(X + Y - \frac{Z}{2})$ is
- If the oxidation state of P in metaphosphate ion, dihydrogen hypophosphite ion and dihydrogen phosphite ion are X , Y and Z respectively. Then value of $\frac{X + Y + Z}{5}$ is
- In cyclotrimetaphosphoric acid $(\text{HPO}_3)_3$ if X is the number of $(p\pi - d\pi)$ multiple bonds, Y is the total number of sp^3 – hybridised atoms and Z is number of sp^2 – hybridised atoms. Then value of $\frac{X + Y - Z}{4}$ is
- In white or yellow phosphorous, calculate the value of expression $\frac{P + Q + R + S}{5}$.

If P = Atomicity of phosphorous,

Q = Total number of vertex angle in phosphorous molecular

R = Total number of P — P bond in phosphorous.

S = Total number of lone pairs in phosphorous molecule.

Exercises

Single Correct Answer Type

Physical Properties

1. Select incorrect statement

- (1) Single N—N bond is stronger than P—P bond.
- (2) PH_3 can act as a ligand in the formation of coordination compound with transition element.
- (3) NO_2 is paramagnetic in nature.
- (4) Covalency of nitrogen in N_2O_5 is four.

2. Reducing power of 15-group hydrides are in order:

- (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
- (2) $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
- (3) $\text{PH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
- (4) $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{NH}_3 > \text{PH}_3$

3. The boiling points of the hydrides of 15-group elements are in the order:

- (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
- (2) $\text{NH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{PH}_3$
- (3) $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
- (4) $\text{AsH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{PH}_3$

4. Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterized compound in +5 oxidation state. The compound is

- (1) Bi_2O_5
- (2) BiF_5
- (3) BiCl_5
- (4) Bi_2S_5

5. In solid state PCl_5 is a

- (1) Covalent solid
- (2) octahedral structure
- (3) Ionic solid $[\text{PCl}_6]^\oplus$ octahedral and $[\text{PCl}_4]^\ominus$ tetrahedral
- (4) Ionic solid with $[\text{PCl}_4]^\oplus$ tetrahedral and $[\text{PCl}_6]^\ominus$ octahedral

6. The boiling point of group 15 follows the order.

- (1) $\text{N} < \text{P} < \text{Bi} < \text{Sb} < \text{As}$
- (2) $\text{P} < \text{N} < \text{As} < \text{Bi} < \text{Sb}$
- (3) $\text{N} < \text{Bi} < \text{P} < \text{Sb} < \text{As}$
- (4) $\text{P} < \text{N} < \text{Bi} < \text{As} < \text{Sb}$

7. Which of the following is the correct order of the thermal stability of hydrides?

- (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
- (2) $\text{PH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
- (3) $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
- (4) $\text{NH}_3 > \text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$

8. The H—M—H bond angle of 15 group hydrides decrease from 107° to 90° from NH_3 to SbH_3 ; this is due to:

- (1) increase in strength to bases with molecular weight
- (2) use of pure p -orbital for M—H bonding in hydrides of higher molecular weight
- (3) bond energies of M—H bonds increase
- (4) bond pairs of electrons go closer to central atom.

9. If X is number of P—O—P bonds in P_4O_{10} and Y is number of P—I bond in solid PI_3 . Then the value of $(X - Y)$ is

- (1) 1
- (2) 2
- (3) 3
- (4) 4

10. Boiling / melting points of the following hydrides follow in order

- (1) $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 < \text{NH}_3$
- (2) $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
- (3) $\text{SbH}_3 > \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$
- (4) $\text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$

11. Anomalous behaviour of nitrogen is due to

- (1) Small size and high EN
- (2) Non-ability of d -orbitals in valence shell
- (3) Ease of multiple bond formation
- (4) All

12. The atomicity of phosphorus is X and the P—P—P bond angle is Y . What are X and Y ?

- (1) $X = 4, Y = 90^\circ$
- (2) $X = 4, Y = 60^\circ$
- (3) $X = 3, Y = 120^\circ$
- (4) $X = 2, Y = 180^\circ$

13. Nitrogen forms N_2 but phosphorus is converted into P_4 from P_2 . The reason for this is

- (1) Triple bond is present between phosphorus atoms
- (2) $p\pi-p\pi$ bonding is weak
- (3) $p\pi-p\pi$ bonding is strong
- (4) Multiple bond is formed easily

14. The element which forms oxides in all the oxidation states from +1 to +5 is

- (1) N
- (2) P
- (3) As
- (4) Sb

Compounds of Nitrogen

15. $p_\pi-p_\pi$ multiple bonding between nitrogen atoms is present in

- (1) hyponitrous acid
- (2) nitrous acid
- (3) nitric acid
- (4) in all of these

16. The nitrogen that decomposes acetylene to cyanogens is

- (1) Dinitrogen
- (2) Active nitrogen
- (3) Passive nitrogen
- (4) Both (2) and (3)

17. Which of the following statements about N_2O is false?

- (1) A neutral oxide which does not form hyponitrous acid with water
- (2) An oily liquid
- (3) Used as propellant for whipped ice-cream
- (4) Used as an anaesthetic

18. Nitrogen dioxide :

- (1) dissolves in water forming HNO_3
- (2) does not dissolve in water
- (3) dissolves in water to form HNO_2 and gives off O_2
- (4) dissolves in water to form a mixture of nitrous and nitric acid

19. It is recommended that liquor ammonia bottle should be opened after cooling it in ice for sometime. This is because liquor ammonia:
- (1) brings tears in the eyes
 - (2) is a corrosive liquid
 - (3) is a mild explosive
 - (4) generates high vapour pressure
20. It is recommended that liquor ammonia bottle should be opened after cooling it in ice for sometime. This is because liquor ammonia:
- (I) The principal reducing product is NO gas
 - (II) Cu metal is oxidised to Cu^{2+} (aq.) ion which is blue in colour.
 - (III) NO is paramagnetic and has one unpaired electron in antibonding molecular orbital
 - (IV) No reacts with O_2 to produce NO_2 which is linear in shape
- Choose the correct statements:
- (1) I, II, III
 - (2) I, III
 - (3) II, IV
 - (4) All the above
21. A brown ring is formed in the ring test for NO_3^- ion. It is due to the formation of
- (1) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$
 - (2) $\text{FeSO}_4 \cdot \text{NO}_2$
 - (3) $[\text{Fe}(\text{H}_2\text{O})_4(\text{NO})_2]^{2+}$
 - (4) $\text{FeSO}_4 \cdot \text{HNO}_3$
22. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from....
- (1) -3 to +3
 - (2) -3 to 0
 - (3) -3 to +5
 - (4) 0 to -3
23. NO_2 is not obtained when following is heated:
- (1) $\text{Pb}(\text{NO}_3)_2$
 - (2) AgNO_3
 - (3) LiNO_3
 - (4) KNO_3
24. Laughing gas is prepared by heating
- (1) $\text{NH}_4\text{Cl} + \text{NaNO}_3$
 - (2) NH_4Cl
 - (3) $(\text{NH}_4)_2\text{SO}_2$
 - (4) NH_4NO_2
25. Which blue-liquid is obtained on reacting equimolar amounts of two gases at -30°C ?
- (1) N_2O
 - (2) N_2O_3
 - (3) N_2O_4
 - (4) N_2O_5
26. Which is the correct sequence in the following properties? For the correct order mark (T) and for the incorrect order mark (F):
- (a) Lewis acidity order : $\text{SiF}_4 < \text{SiCl}_4 < \text{SiBr}_4 < \text{SiI}_4$
 - (b) Melting point : $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 - (c) Boiling point : $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 - (d) Bond dipole order : $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
- (1) FTFT
 - (2) TFTF
 - (3) FFTT
 - (4) FFTF
27. An orange solid (X) on heating gives a colourless gas (Y) and only a green residue (Z). Gas (Y) on treatment with Mg produces a white solid substance:
- (1) Mg_3N_2
 - (2) MgO
 - (3) Mg_2O_3
 - (4) MgCl_2
28. Calcium imide on hydrolysis will give gas (B) which on oxidation by bleaching powder given gas (C). Gas (C) on reaction with magnesium gives compound (D). (D) on hydrolysis gives again gas (B). (B), (C) and (D) are:
- (1) NH_3 , N_2 , Mg_3N_2
 - (2) N_2 , NH_3 , MgNH
 - (3) N_2 , N_2O_5 , $\text{Mg}(\text{NO}_3)_2$
 - (4) NH_3 , NO_2 , $\text{Mg}(\text{NO}_2)_2$
29. Among the following compounds, which on heating do not produce N_2 ?
- (1) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 - (2) $\text{NH}_4\text{Cl} + \text{NaNO}_2$
 - (3) $\text{NH}_4\text{Cl} + \text{CaO}$
 - (4) $\text{Ba}(\text{N}_3)_2$
30. Nitrogen (I) oxide is produced by:
- (1) thermal decomposition of sodium nitrite at low temperature
 - (2) thermal decomposition of ammonium nitrite
 - (3) disproportionation of N_2O_4
 - (4) interaction of hydroxyl amine and nitrous acid
31. Match List-I with List-II and select the correct answer using the codes given below the lists:
- | List-I (Compounds) | | List-II (used in) | |
|----------------------------------|-----|------------------------------------|-----|
| (A) $\text{BaSO}_4 + \text{ZnS}$ | | (1) Explosive | |
| (B) NI_3 | | (2) Oxidiser in rocket propellants | |
| (C) N_2O_4 | | (3) Space capsule | |
| (D) KO_2 | | (4) Pigment | |
| (A) | (B) | (C) | (D) |
| (1) 3 | 1 | 4 | 2 |
| (2) 4 | 1 | 2 | 3 |
| (3) 3 | 4 | 1 | 2 |
| (4) 4 | 3 | 2 | 1 |
32. Which of the following compound does not produce oxyacid of central atom on hydrolysis?
- (1) BF_3
 - (2) NCl_3
 - (3) SF_4
 - (4) PCl_5
33. The INCORRECT statement regarding 15th group hydrides (EH_3). [$E = \text{N, P, As, Sb, Bi}$]
- (1) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$: Thermal stability
 - (2) $\text{N}-\text{H} > \text{P}-\text{H} > \text{As}-\text{H} > \text{Sb}-\text{H} > \text{Bi}-\text{H}$: E—H bond dissociation enthalpy
 - (3) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$: Reducing character
 - (4) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$: Basicity
34. Which of the following oxyacid contains both P—H and P—P bond simultaneously?
- (1) $\text{H}_4\text{P}_2\text{O}_5$
 - (2) $\text{H}_4\text{P}_2\text{O}_7$
 - (3) $\text{H}_4\text{P}_2\text{O}_6$
 - (4) None

35. Among the following statement which one is true?
 (1) NH_3 is less soluble than PH_3 in water
 (2) NH_3 is stronger base and stronger reducing agent than PH_3
 (3) NH_3 has higher boiling point than PH_3 and has lower melting point than PH_3
 (4) PH_3 is stronger reducing agent than NH_3 and it has lower critical temperature than NH_3
36. Which of the following statements regarding N_2O_4 is NOT CORRECT?
 (1) It is a planar molecule
 (2) It is used as non-aqueous solvent
 (3) It involves $\text{N}-\text{N}$ bond which is larger than the $\text{N}-\text{N}$ bond in hydrazine
 (4) Ammonium nitrate in N_2O_4 acts as a base
37. Which of the following on heating produces NO_2 ?
 (1) NaNO_3 (2) AgNO_3
 (3) NH_4NO_3 (4) NH_4NO_2
38. Which of the following equation is wrong ?
 (1) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$
 (2) $\text{I}_2 + 10\text{HNO}_3 \longrightarrow 2\text{HIO}_4 + 10\text{NO}_2 + 4\text{H}_2\text{O}$
 (3) $\text{S} + 6\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$
 (4) None of the above
39. Nitrogen gas is liberated by thermal decomposition of:
 (1) NH_4NO_2 (2) NaN_3
 (3) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (4) All
40. Two oxides of nitrogen, NO and NO_2 are allowed to react together at 243°K and form a coloured compound of nitrogen (X). When compound (X) reacts with water to yield another compound of nitrogen (Y). The shape of the anion of (Y) molecule is:
 (1) triangular planar (2) triangular pyramidal
 (3) tetrahedron (4) square planar
41. Consider the following sequence of reaction.

$$\text{Na} + \text{NH}_3(\text{g}) \longrightarrow [\text{X}] \xrightarrow{\text{N}_2\text{O}} [\text{Y}] \xrightarrow{\text{Heat}} [\text{Z}]$$
 Gas Pure
 Identify $[\text{Z}]$ gas:
 (1) N_2 (2) NH_3
 (3) O_2 (4) H_2
42. $\text{NH}_3 + \text{O}_2 \xrightarrow[\Delta]{\text{Pt}} \text{A} + \text{H}_2\text{O}$;
 $\text{A} + \text{O}_2 \longrightarrow \text{B}$;
 $\text{B} + \text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{C}$;
 A , B and C are:
 (1) N_2O , NO_2 and HNO_3 (2) NO , NO_2 and HNO_3
 (3) NO_2 , NO and HNO_3 (4) N_2O , NO and HNO_3
43. The mixed anhydride of nitrous and nitric acid is
 (1) N_2O (2) NO_2
 (3) NO (4) N_2O_5
44. Copper reacts with dil. HNO_3 to form a nitrate and
 (1) NO_2 (2) NO
 (3) N_2O_3 (4) N_2O_5
45. Nitrogen sesquioxide is
 (1) N_2O_3 (2) N_2O_4
 (3) N_2O_5 (4) N_2O
46. When silver nitrate is heated, the products are
 (1) Oxygen and metal nitrite
 (2) Nitrogen dioxide, O_2 and metallic oxide
 (3) Nitrogen dioxide, O_2 and metal
 (4) Nitrogen dioxide and metal oxide
47. NO is purified by
 (1) Absorption in $(\text{NH}_4)_2\text{SO}_4$ solution
 (2) Passing into conc. H_2SO_4
 (3) Absorbing in FeSO_4 solution
 (4) Electrolysis method
48. Which of the following combines with Fe^{2+} ions to form brown complex?
 (1) NO (2) N_2O
 (3) N_2O_3 (4) N_2O_5
49. Nitrogen reacts with calcium and carbon or when N_2 gas is passed over heated calcium carbide (at 1070 K) it gives _____ which is an important fertiliser marketed under the name Nitrolim
 (1) Calcium nitrate (2) Calcium cyanide
 (3) Calcium cyanamide (4) Calcium nitride
50. Ordinary strong solution of HCl , HNO_3 and H_2SO_4 contains roughly
 (1) $1/5$, $2/3$ and $3/3$ fractions of pure acid and water respectively
 (2) $2/3$, $1/5$ and $3/3$ fractions of pure acid and water respectively
 (3) $2/3$, $3/3$ and $1/5$ fractions of pure acid and water respectively
 (4) None
51. Dilute HNO_3 cannot be concentrated beyond 68% by boiling because
 (1) On boiling HNO_3 is decomposed
 (2) On boiling HNO_3 produces a large amount of heat which is uncontrollable
 (3) It forms a constant boiling mixture with H_2O boiling at 394 K
 (4) It can be concentrated beyond 68% by steam distillation
52. Fuming HNO_3 (containing 98% of HNO_3) is obtained
 (1) By distilling 68% HNO_3 with conc. H_2SO_4
 (2) By distilling 68% HNO_3 under reduced pressure
 (3) By steam distillation of 68% HNO_3
 (4) By distillation 68% HNO_3 with P_4O_{10}
53. Nitrolim is
 (1) CaCN_2 (2) $\text{CaCN}_2 + \text{C}$
 (3) CaC_2 (4) $\text{CaCN}_2 + \text{CaC}_2$

54. Nitrochalk is

- (1) CAN (2) CaNCN
(3) $(\text{NH}_4)_2\text{SO}_4$ (4) $\text{Ca}(\text{NO}_3)_2 \cdot \text{CaO}$

55. Which of the following acid posses oxidising, reducing and complex forming properties?

- (1) HNO_3 (2) HNO_2
(3) H_2SO_4 (4) HCl

56. Acidic hydride of nitrogen is

- (1) NH_3 (2) N_3H
(3) N_2H_4 (4) N_2H_2

57. Which one of the following pairs is obtained on heating ammonium dichromate?

- (1) N_2 and H_2O (2) N_2O and H_2O
(3) NO and H_2O (4) NO and NO_2

58. In salt which on heating gives a mixture of two gases is

- (1) NaNO_3 (2) KNO_3
(3) $\text{Pb}(\text{NO}_3)_2$ (4) NH_4NO_3

59. When ammonia is heated with CO_2 under pressure, the product is

- (1) $(\text{NH}_4)_2\text{CO}_3$ (2) NH_2CONH_2
(3) $\text{NH}_2\text{COONH}_4$ (4) NH_4HCO_3

60. When treated with nitric acid which of the following liberates hydrogen?

- (1) Zinc (2) Copper
(3) Magnesium (4) Mercury

61. The reaction between $\text{NH}_2^\ominus$ and N_2O gives

- (1) NO (2) N_2O_5
(3) NH_2NH_2 (4) $\text{N}_3^\ominus$

62. Hydrolysis of NCl_3 gives NH_3 and X. Which of the following is X?

- (1) HClO_4 (2) HClO_3
(3) HOCl (4) HClO_2

63. Chlorine reacts with excess of ammonia to form

- (1) NH_4Cl (2) $\text{N}_2 + \text{HCl}$
(3) $\text{N}_2 + \text{NH}_4\text{Cl}$ (4) $\text{N}_2 + \text{NCl}_3$

64. In $\text{NO}_3^\ominus$ ion, the number of bond pair and lone pair of electrons on nitrogen atoms are

- (1) 2, 2 (2) 3, 1
(3) 1, 3 (4) 4, 0

65. A pale blue liquid which is obtained by reacting equimolar mixture of two gases at -30°C is

- (1) N_2O_3 (2) N_2O
(3) N_2O_4 (4) N_2O_5

66. The INCORRECT order is:

- (1) Thermal stability : $\text{HF} > \text{HCl} > \text{HBr}$
(2) Lewis basic character: $\text{PF}_3 < \text{PCl}_3 < \text{PBr}_3$
(3) % *p*-character : $\text{NO}_2^+ > \text{NO}_3^- > \text{NH}_4^+$
(4) Bond angle : $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

Compounds of Phosphorous

67. Calculate $x + y + z$ for H_3PO_3 acid, where x is number of lone pairs, y is number of σ -bonds and z is number of π -bonds:

- (1) 5 (2) 14
(3) 13 (4) 12

68. A non-metal M forms $M\text{Cl}_3$, $M_2\text{O}_5$ and Mg_3M_2 but does not form $M\text{I}_5$. Then incorrect statement regarding non-metal M is:

- (1) M can form multiple bond
(2) M is of second period element
(3) Atomicity of non-metal is 4
(4) The range of oxidation number for M is +5 to -3

69. The formation of $\text{PH}_4^\oplus$ is difficult compared to $\text{NH}_4^\oplus$ because:

- (1) lone pair of phosphorus is optically inert
(2) lone pair of phosphorus resides in almost pure *p*-orbital
(3) lone pair of phosphorus resides at sp^3 orbital
(4) lone pair of phosphorus resides in almost pure *s*-orbital

70. In a cyclotrimetaphosphoric acid molecule, how many single and double bonds are present?

- (1) 3 double bonds; 9 single bonds
(2) 6 double bonds; 6 single bonds
(3) 3 double bonds; 12 single bonds
(4) Zero double bonds; 12 single bonds

71. Amongst the following compounds

- (I) $\text{H}_5\text{P}_3\text{O}_{10}$ (II) $\text{H}_6\text{P}_4\text{O}_{13}$
(III) $\text{H}_5\text{P}_5\text{O}_{15}$ (IV) $\text{H}_7\text{P}_5\text{O}_{16}$

non-cyclic phosphates are:

- (1) I, III (2) I, II, III
(3) I, II, IV (4) I, II, III, IV

72. Strong reducing behaviour of H_3PO_2 is due to

- (1) Low oxidation state of phosphorus
(2) Presence of two $-\text{OH}$ Group and one $\text{P}-\text{H}$ bonds
(3) Presence of one $-\text{OH}$ group and two $\text{P}-\text{H}$ bonds
(4) High electron gain enthalpy of phosphorus

73. The cyclotrimetaphosphoric acid is:

- (1) $(\text{HPO}_3)_3$ and contains 9 σ -bonds
(2) $\text{H}_3\text{P}_3\text{O}_6$ and contains 12 σ -bonds
(3) $(\text{HPO}_3)_3$ and contains 15 σ -bonds
(4) $\text{H}_3\text{P}_3\text{O}_6$ and contains 18 σ -bonds

74. Which of the following acids forms three series of salts?

- (1) H_3PO_2 (2) H_3PO_2
(3) H_3PO_4 (4) H_3PO_3

75. $\text{A} + \text{H}_2\text{O} \longrightarrow 6 + \text{HCl}$

$\text{B} + \text{H}_2\text{O} \longrightarrow \text{C} + \text{HCl}$

Compound (A), (B) and (C) will be respectively:

- (1) PCl_5 , POCl_3 , H_3PO_3 (2) PCl_5 , POCl_3 , H_3PO_4
(3) SOCl_2 , POCl_3 , H_3PO_3 (4) PCl_3 , POCl_3 , H_3PO_4

76. The product formed in the reaction of SOCl_2 with white phosphorus is:

- I. PCl_3 II. SO_2 III. S_2Cl_2 IV. POCl_3

- (1) I, II, III (2) II, III, IV
(3) I, II (4) III, IV

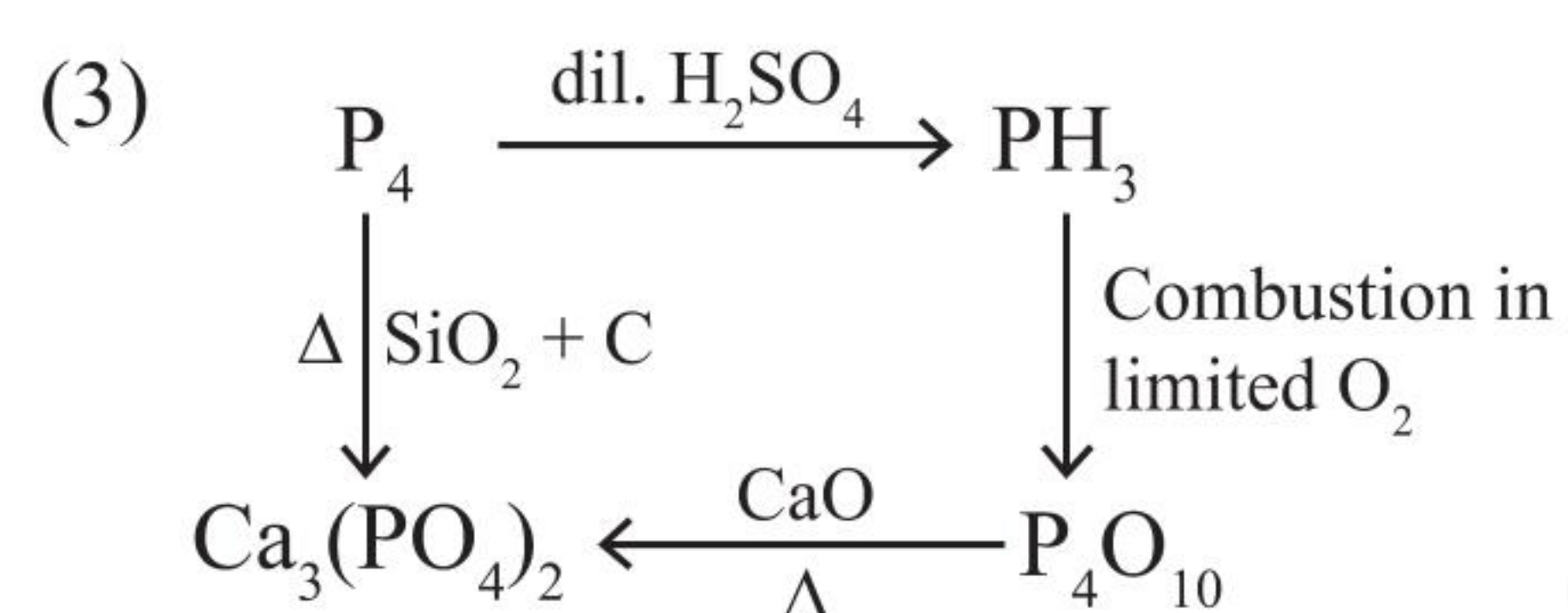
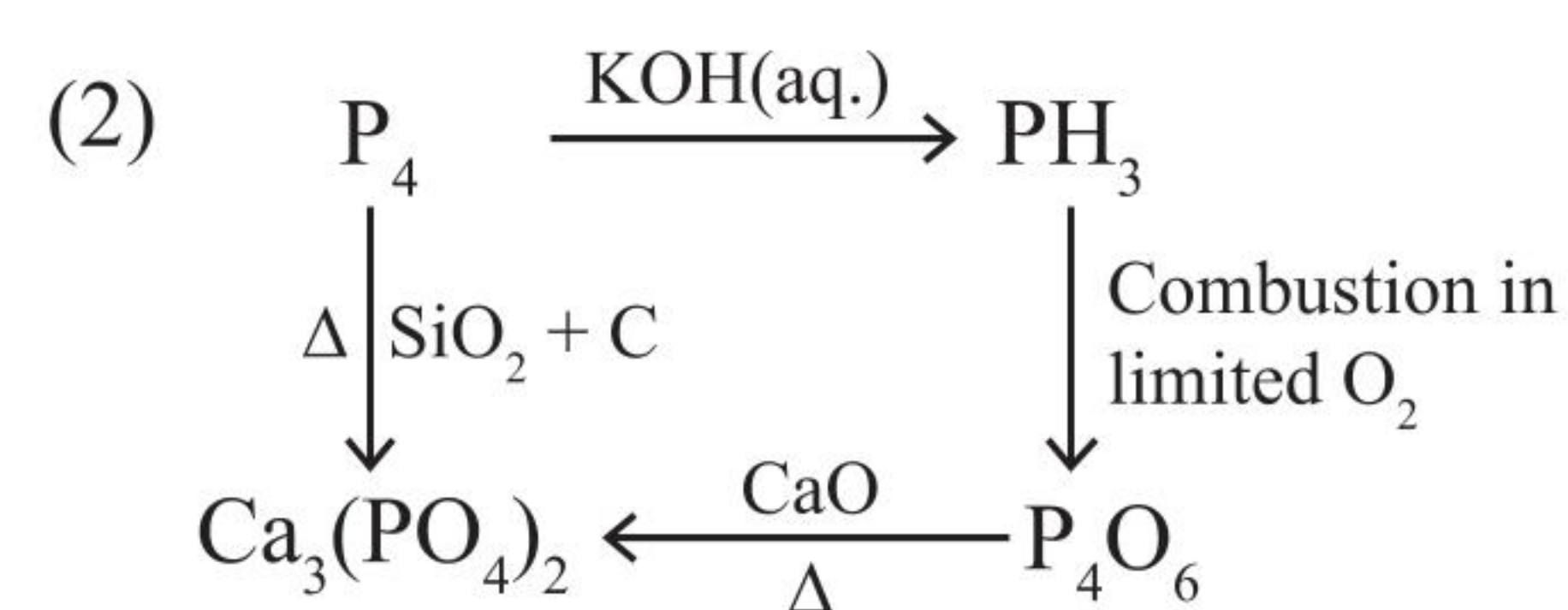
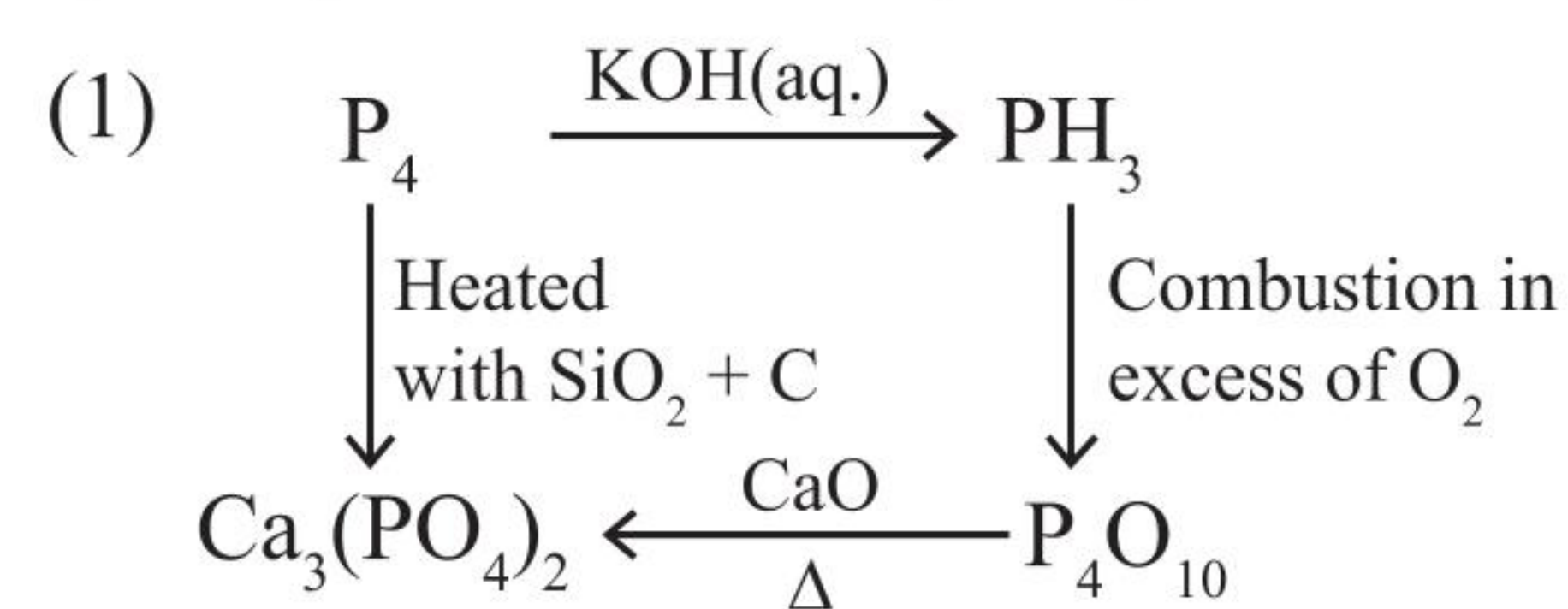
77. In which of the following compounds hydrolysis takes place through $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ mechanism respectively?

- (1) NF_3 , NCl_3 (2) P_4O_{10} , SiCl_4
(3) SF_6 , TeF_6 (4) SiCl_4 , SiF_4

78. Incorrect statement about PH_3 is:

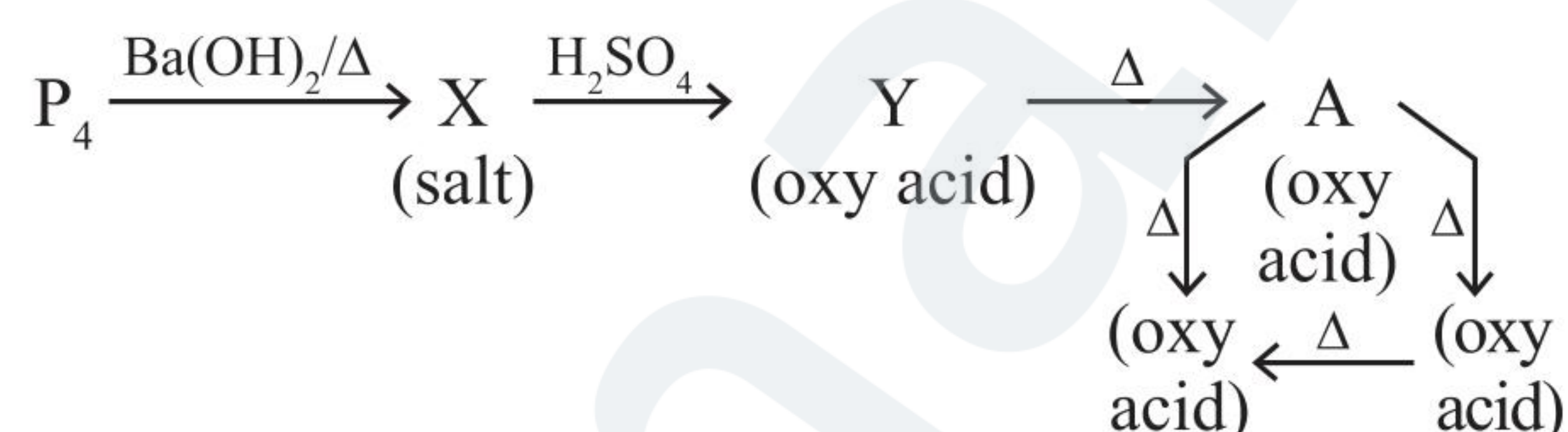
- (1) It is produced by hydrolysis of Ca_3P_2
(2) It gives black ppt. (Cu_3P_2) with CuSO_4 solution
(3) Spontaneously burns in presence of P_2H_4
(4) It does not react with B_3H_6

79. Which of the following reacting sequence is correct regarding conversion of phosphorus compounds?



(4) None of these.

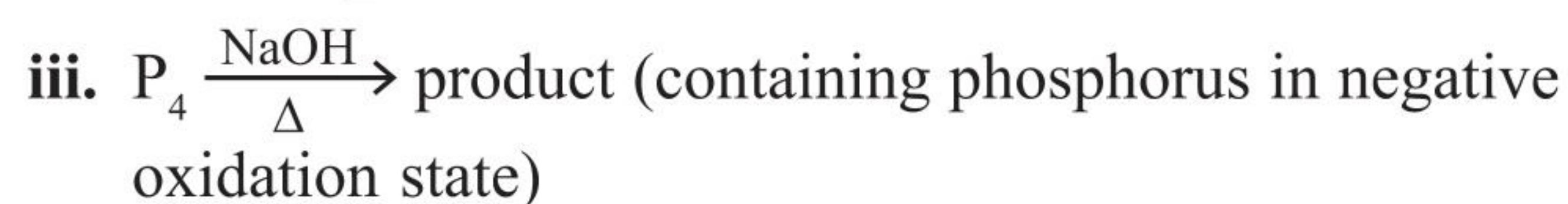
80. Consider the following sequence of reaction:



In the above sequence of reactions Y and A are respectively:

- (1) H_3PO_2 and H_3PO_4 (2) H_3PO_4 and $\text{H}_3\text{P}_2\text{O}_7$
(3) H_3PO_4 and HPO_3 (4) H_3PO_3 and H_3PO_4

81. Consider the following reactions:



The order of change in bond angle (for reactant $\rightarrow$ specified product) is:

- (1) (i) > (ii) > (iii) (2) (ii) > (iii) > (i)
(3) (iii) > (ii) > (i) (4) (ii) > (i) > (iii)

82. In which of the following acids, P—P bonds is present?

- (1) Tetra poly phosphoric acid ($\text{H}_6\text{P}_4\text{O}_{13}$)
(2) Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$)
(3) Hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$)
(4) Polymetaphosphoric acid (HPO_3)_n

83. Of the following the most acidic is

- (1) H_3PO_4 (2) H_3AsO_4
(3) H_3SbO_4 (4) H_3BiO_4

84. Which of the following form maximum P—H bonds?

- (1) H_3PO_2 (2) H_3PO_4
(3) H_3PO_3 (4) $\text{H}_4\text{P}_2\text{O}_7$

85. PCl_5 in solid state exists as

- (1) PCl_5 (2) PCl_4^+
(3) PCl_6^- (4) $\text{PCl}_4^+ \text{PCl}_6^-$

86. Graham's salt used for softening of water and with other alkalis used for cleaning sinks, drains and floors is

- (1) $(\text{NaPO}_3)_n$ (2) $(\text{KPO}_3)_n$
(3) Na_3PO_4 (4) K_3PO_4

87. The structure of phosphide ion is similar to that of

- (1) Nitride ion (2) Chloride ion
(3) Fluoride ion (4) Sodium ion

88. Calcium phosphide is used in smoke screen because it

- (1) Burns to form soot
(2) Gives phosphine which catches fire to give needed smoke
(3) Immediately catches fire in air
(4) Is a gas which brings tears in the eyes

89. Holme's signals produce burning gases which serve as a signal to the approaching ships contains

- (1) A mixture of Ca_3P_2 and CaC_2
(2) A mixture of Ca_3P_2 and KOH
(3) A mixture of CaC_2 and KOH
(4) A mixture of Ca_3P_2 , CaC_2 and KOH

90. PCl_3 , P_4O_6 and P_4O_{10} , PCl_5 on hydrolysis gives respectively

- (1) H_3PO_3 and H_3PO_4 (2) H_3PO_4 and H_3PO_3
(3) $(\text{HPO}_3)_n$ and $\text{H}_4\text{P}_2\text{O}_7$ (4) $\text{H}_4\text{P}_2\text{O}_7$ and $(\text{HPO}_3)_n$

91. The number of P—O—P and P—OH bonds present respectively in pyrophosphoric acid molecule are

- (1) 2, 3 (2) 1, 8
(3) 1, 4 (4) 1, 2

92. When phosphine is bubbled through a solution of nitrate _____ is precipitated.

- (1) Silver (2) Silver phosphide
(3) Silver oxide (4) None of these

93. When orthophosphoric acid is heated at 240°C , the main product formed is

- (1) H_3PO_3 (2) H_3PO_2
(3) HPO_3 (4) $\text{H}_4\text{P}_2\text{O}_7$

94. White phosphorus reacts with caustic soda. The products are PH_3 and NaH_2PO_2 . This reaction is an example of
 (1) Oxidation (2) Reduction
 (3) Neutralisation (4) Disproportionation
95. The number of P—O—P bridges in the structure of P_4O_{10} and P_4O_6 are respectively
 (1) 5, 5 (2) 5, 6
 (3) 6, 6 (4) 6, 5
96. Cl—P—Cl bond angles in PCl_5 molecule are
 (1) 120° and 90° (2) 60° and 90°
 (3) 60° and 120° (4) 120° and 30°
97. Scheel's green, formerly used as a green pigment for colouring wall paper is
 (1) Sodium arsenite (Na_3AsO_3)
 (2) Cupric arsenite (CuHAsO_3)
 (3) Silver arsenite (Ag_3AsO_3)
 (4) None
98. Paris green was used as a pigment due to unique light green colour but now-a-days it is used as an insecticide. It is prepared by boiling verdigris (basic acetate of copper), arsenious oxide and acetic acid together. It is
 (1) $(\text{CH}_3\text{COO})_2\text{Cu} \cdot 3\text{Cu}(\text{AsO}_2)_2$
 (2) Cupric acetoarsenite
 (3) $\text{Cu}_4(\text{CH}_3\text{COO})_2(\text{AsO}_2)_2$
 (4) All
99. Tartar emetic (potassium antimony tartrate) is used as an emetic in small doses while larger doses are poisonous. It is used for the treatment of Kala-azar and such other tropical diseases. It is formed when antimony trioxide (Sb_2O_3) is treated with potassium hydrogen tartrate. It is
- | | |
|--|---|
| (1) $\begin{array}{c} \text{CH(OH) COO (SbO)} \\ \\ \text{CH(OH) COOK} \end{array}$ | (2) $\begin{array}{c} \text{CH(OH) COO (Sb)} \\ \\ \text{CH(OH) COOK} \end{array}$ |
| (3) $\begin{array}{c} \text{CH(OH) COO (Sb}_2\text{O}_3) \\ \\ \text{CH(OH) COOK} \end{array}$ | (4) $\begin{array}{c} \text{CH(OH) COO (SbO}_3) \\ \\ \text{CH(OH) COOK} \end{array}$ |
100. Which one of the following halide does not hydrolyse?
 (1) SbCl_3 (2) AsCl_3
 (3) PCl_3 (4) NF_3
101. Wittig reagent is used for the synthesis of alkenes from ketone in organic chemistry. The Wittig reagent is
 (1) $(\text{Ph}_3\text{P})=\text{CH}_2$ Triphenyl phosphine methylene
 (2) $(\text{Ph}_3\text{P})=\text{O}$ Triphenyl phosphine oxide
 (3) $(\text{Ph}_3\text{P})\text{CH}_3\text{Br}$
 (4) Ph_3P
102. Following tests are shown by
 i. Decolourisation of acidified soln. of KMnO_4
 ii. Liberation of I_2 from an acidified soln. of KI
 iii. On treatment with dil HCl , brown fumes of NO_2 which turns FeSO_4 soln. black
- (1) Nitrites (2) Nitrates
 (3) Both (1) and (2) (4) Neither (1) nor (2)
103. PCl_5 exist but NCl_5 does not because
 (1) NCl_5 is unstable
 (2) Nitrogen has no vacant orbitals
 (3) Nitrogen atom is much smaller
 (4) Nitrogen is highly inert
104. PCl_5 and PH_3 exist but PH_5 does not because
 (1) PH_5 is unstable
 (2) Phosphorous has no vacant orbitals
 (3) Phosphorous exists as P_4
 (4) EN of hydrogen is less as compared to chlorine to excite electron from p orbital to d orbital for bond formation
105. N_2 forms NCl_3 whereas P can form both PCl_3 and PCl_5 . Why?
 (1) P has d -orbitals which can be used for bonding but N does not have
 (2) N atom is larger than P in size
 (3) P is more reactive towards Cl than N
 (4) None of the above
106. The following are some statements related to group 15 hydrides
 i. Reducing property increases from NH_3 to BiH_3
 ii. Tendency to donate lone pair decreases from NH_3 to BiH_3
 iii. Thermal stability of hydrides decreases from NH_3 to BiH_3
 iv. Bond angle decreases from NH_3 to BiH_3
 The correct statements are:
 (1) (i), (ii), (iii) and (iv) (2) (i), (iii) and (iv)
 (3) (i), (ii) and (iv) (4) (i) and (iv)
107. Phosphine, acetylene and ammonia can be formed by treating water with
 (1) Mg_3P_2 , Al_4C_3 , Li_3N (2) Ca_3P_2 , CaC_2 , Mg_3N_2
 (3) Ca_3P_2 , CaC_2 , CaCN_2 (4) Ca_3P_2 , Mg_2C , NH_4NO_3
108. $\text{Th CN}^\ominus$ ion and N_2 are isoelectronic. But in contrast to $\text{CN}^\ominus$, N_2 is chemically inert because of
 (1) Low bond energy
 (2) Absence of bond polarity
 (3) Unsymmetrical electron distribution
 (4) Presence of more number of electrons in bonding orbitals
109. White phosphorus on reaction with lime water gives calcium salt of an acid (A) along with a gas (X). Which of the following is correct?
 (1) (A) on heating gives (X) and O_2
 (2) The bond angle in (X) is less than that in case of ammonia
 (3) (A) is a dibasic acid
 (4) (X) is more basic than ammonia

110. One mole of H_3PO_3 on reaction with excess of NaOH gives:
 (1) One mole of Na_2HPO_3 (2) Two moles of $\text{Na}_2\text{H}_2\text{PO}_3$
 (3) Two moles of Na_2HPO_3 (4) One mole of Na_3PO_3
111. If O_2 is removed from the formula of anhydride of HNO_2 , then the formula of the resulting compound satisfies which of the following properties?
 (1) It produces tears in eyes
 (2) It supports combustion
 (3) It is paramagnetic
 (4) It cannot react with red hot copper
112. Which of the following statements is correct?
 (1) N_2O is a laughing gas and is angular in shape
 (2) NO_2 is a sweet smelling and is angular in shape
 (3) NO is a colourless gas and acidic in nature
 (4) NO_2 on reaction with NaOH gives a mixture of two Salts
113. The compound is covalent in gaseous state but ionic in solid state is
 (1) PCl_5 (2) PCl_3
 (3) CCl_4 (4) NH_3
114. The equivalent mass of phosphoric acid (H_3PO_4) in reaction, $\text{NaOH} + \text{H}_3\text{PO}_4 \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$, is
 (1) 29 (2) 49
 (3) 59 (4) 98
115. The oxyacid of phosphorus in which phosphorus has lowest oxidation state is
 (1) Hypophosphorus acid (2) Orthophosphoric acid
 (3) Pyrophosphoric acid (4) Metaphosphoric acid
116. Which is/are correct statements about P_4O_6 and P_4O_{10} :
 (1) In P_4O_6 each P is joined to three O and in P_4O_{10} each P is linked to four O atoms.
 (2) Both form oxoacids H_3PO_3 and H_3PO_4 respectively
 (3) Both (1) and (2)
 (4) None
117. Blue liquid which is formed at -30°C by mixing of two gases is
 (1) N_2O (2) N_2O_4
 (3) N_2O_3 (4) N_2O_5
3. Which is true about N_2O_5 ?
 (1) It is anhydride of HNO_3
 (2) In solid state it exists as $\text{NO}_2^+ \text{NO}_3^-$
 (3) It is structurally similar to P_2O_5
 (4) It can be prepared by heating HNO_3 over P_2O_5
4. Orthophosphoric acid $\xrightarrow[220^\circ\text{C}]{\text{gentle heat}} \text{P}$
 What is/are correct about P?
 (1) It is a tetrabasic acid
 (2) It contains one $\text{P} - \text{O} - \text{P}$ bond
 (3) It is a dibasic acid
 (4) On hydrolysis it produces metaphosphoric acid
5. At high temperatures, nitrogen directly does not combine with:
 (1) Zn (2) Mg
 (3) Al (4) Fe
6. Which product(s) is not obtained in the following reaction?
 $\text{P} + \text{OH} \longrightarrow \text{Product(s)}$
 (1) PH_3 (2) PO_4^{2-}
 (3) H_2PO_2^- (4) PO_2^-
7. Phosphine is not obtained by the reaction when:
 (1) White phosphorus is heated with NaOH
 (2) Ca_3P_2 reacts with water
 (3) red phosphorus is heated with NaOH
 (4) phosphorus is heated in current of hydrogen
8. Which of the following statements is/are incorrect?
 (1) NO_2 is a diamagnetic substance
 (2) Solid is brown in colour
 (3) NO_2 dimerizes to N_2O_4
 (4) NO_2 is a mixed anhydride
9. Which of the following statements are true about P_4O_6 and P_4O_{10} ?
 (1) Both these oxides have a closed cage like structure
 (2) Each oxide requires 6 water molecules for complete hydrolysis to form their respective oxoacids
 (3) Both these oxides contain 12 equivalent $\text{P} - \text{O}$ bonds
 (4) P_4O_6 and P_4O_{10} both contain $\text{p}\pi - \text{d}\pi$ bonds
10. Which of the following, when dissolved in water, will liberate ammonia?
 (1) NaNO_3 (2) NaNO_2
 (3) NaNH_2 (4) Na_3N_2
11. Which of the following is not true for allotropes of phosphorus?
 (1) Yellow phosphorus is soluble in CS_2 while red phosphorus is not
 (2) $\text{P} - \text{P} - \text{P}$ bond angle is 60° in red phosphorus
 (3) On heating in air, white phosphorus changes to red
 (4) White phosphorus slowly changes to red phosphorus at ordinary temperatures

Multiple Correct Answers Type

Physical Properties

1. Which of the following act as an oxidising as well as a reducing agent?
 (1) HNO_2 (2) H_2O_2
 (3) H_2S (4) SO_2
2. White phosphorus cannot be separated from red phosphorus by:
 (1) sublimation (2) dissolving in CS_2
 (3) distillation (4) heating and alkali solution

12. PH_3 can be obtained by:
- (1) heating hypophosphorus acid
 - (2) heating orthophosphorus acid
 - (3) reaction of P_4 with hot conc. NaOH
 - (4) hydrolysis of calcium phosphide
13. Select the correct trends.
- (1) $\text{N} < \text{P} < \text{Bi} < \text{Sb} < \text{As}$ (Melting point)
 - (2) $\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$ (Ionisation energy)
 - (3) $\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$ (Electronegativity)
 - (4) $\text{P} < \text{N} < \text{As} < \text{Bi} < \text{Sb}$ (Melting point)
14. Which of the following statements are INCORRECT?
- (1) The number of $\text{P} - \text{O} - \text{P}$ bond in P_4O_6 , P_4O_8 and P_4O_{10} are equal in number.
 - (2) P_4O_8 and P_4O_{10} have 5 $\text{P} - \text{O} - \text{P}$ bonds
 - (3) P_4O_{10} has 4 ' $-\text{P}=\text{O}$ '
 - (4) P_4O_6 and P_4O_8 have zero and two $-\text{P}=\text{O}$ bonds respectively.
15. Which of the following orders are correct according to indicated property?
- (1) $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_4 < \text{N}_2\text{O}_5$ (strength of oxides of nitrogen)
 - (2) P_4O_6 and $\text{N}_2\text{O}_3 < \text{As}_4\text{O}_6 > \text{Sb}_4\text{O}_6$ (acidic strength of trioxides)
 - (3) $\text{N}_2\text{O}_5 > \text{P}_4\text{O}_{10} > \text{As}_4\text{O}_{10} > \text{Sb}_4\text{O}_6$ (acidic strength of pentoxides)
 - (4) $\text{PI}_3 < \text{PBr}_3 > \text{PCl}_3 > \text{PF}_3$ (Bond angle)
16. Choose the correct statements
- (1) $\text{NF}_3 < \text{NCl}_3 < \text{NBr}_3 < \text{NI}_3$ (Lewis base strength)
 - (2) In hydrolysis of SbCl_3 , the addition of excess of HCl suppresses the hydrolysis by shifting the equilibrium to the left
 - (3) NF_3 does not undergo hydrolysis
 - (4) Thermal stability of $\text{PCl}_3 > \text{PCl}_5$
17. Which of the following statements are incorrect?
- (1) All the three $\text{N} - \text{O}$ bond length in HNO_3 are equal
 - (2) All $\text{P} - \text{C}$ bond length in PCl_5 molecule in gaseous state are equal
 - (3) P_4 molecule in white phosphorus have angular strain therefore white phosphorus is very reactive
 - (4) PCl_5 is ionic in solid state in which cation is octahedral and anion tetrahedral
- Compounds of Nitrogen**
18. Which of the following compounds is NOT obtained when HNO_3 reacts with P_4O_{10} ?
- (1) N_2O_5
 - (2) NO_2
 - (3) NO
 - (4) HPO_3
19. Which of the following compound(s) are explosive(s)?
- (1) NCl_3
 - (2) NI_3
 - (3) NBr_3
 - (4) NF_3
20. The following side reaction in the production of N_2H_4
- $$\text{N}_2\text{H}_4 + 2\text{NH}_2\text{Cl} \longrightarrow \text{N}_2 + 2\text{NH}_4\text{Cl}$$
- (1) is catalysed by traces of heavy metals as Cu^{2+}
 - (2) is suppressed by addition of gelatin or glue
 - (3) is made reversible by removing N_2
 - (4) is made reversible by adding NaOH
21. The nitrogen oxide(s) that contain (s) $\text{N}-\text{N}$ bond(s) is (are)
- (1) N_2O
 - (2) N_2O_3
 - (3) N_2O_4
 - (4) N_2O_5
22. N_2H_4 reduces IO_3^-/H^+
- (1) to I^+
 - (2) with I_2 as an intermediate indicated by violet colour in CCl_4 layer
 - (3) indicated by blue colour with starch
 - (4) to I^-
23. Ammonia reacts with Nessler's reagents to give a brown ppt. due to formation of
- (1) $\text{H}_2\text{N}-\text{Hg}-\text{O}-\text{HgI}$
 - (2) IO_3^-
 - (3) Iodide of Millon's base
 - (4) K_2HgI_4
24. Which of the following are used as fertilizers?
- (1) $\text{Ca}_3(\text{PO}_4)_2$
 - (2) $\text{Ca}(\text{H}_2\text{PO}_4)_2$
 - (3) CaNCN
 - (4) CaC_2
25. Photochemical decomposition of HNO_3 produces:
- (1) N_2
 - (2) N_2O
 - (3) NO_2
 - (4) O_2
26. Which of the following statement(s) regarding nitrogen sesquioxide (N_2O_3) is/are correct?
- (1) Nitrogen sesquioxide is stable only in the liquid state. It dissociates in the vapour state
 - (2) Nitrogen sesquioxide is a neutral oxide
 - (3) Nitrogen sesquioxide contains a weak $\text{N}-\text{N}$ bond
 - (4) Nitrogen sesquioxide exists in two different forms
27. Select the correct reaction(s)
- (1) $\text{NH}_4\text{NO}_3 \xrightarrow{250^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
 - (2) $\text{NH}_2\text{OH} + \text{HNO}_2 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
 - (3) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$
 - (4) $\text{As}_2\text{O}_3 + \text{HNO}_3(\text{dil}) \longrightarrow \text{N}_2\text{O}_3 + 2\text{H}_3\text{AsO}_4$
28. The metals which produce hydrogen only with very dilute nitric acid are
- (1) Zn
 - (2) Cu
 - (3) Mg
 - (4) Mn
29. The nitrogen oxide(s) that contain(s) $\text{N}-\text{N}$ bond(s) is(are)
- (1) N_2O
 - (2) N_2O_3
 - (3) N_2O_4
 - (4) N_2O_5
30. A solution of colourless salt on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) is (are)

- (1) NH_4NO_3 (2) NH_4NO_2
 (3) NH_4Cl (4) $(\text{NH}_4)_2\text{SO}_4$

Compounds of Phosphorous

31. Which of the following are similarities between $\text{H}_4\text{P}_4\text{O}_{12}$ and $\text{H}_4\text{P}_2\text{O}_7$?

- (1) Structure
 (2) Total number of atoms directly bonded by each phosphorous atom
 (3) Type of linkage (X—O—X/X—X)
 (4) Number of P—O—P linkage

32. PCl_5 is formed when:

- (1) white phosphorus reacts with limited dry chlorine
 (2) white phosphorous reacts with excess of dry chlorine
 (3) white phosphorus reacts with excess of SO_2Cl_2
 (4) white phosphorus reacts with excess of SO_2Cl_2

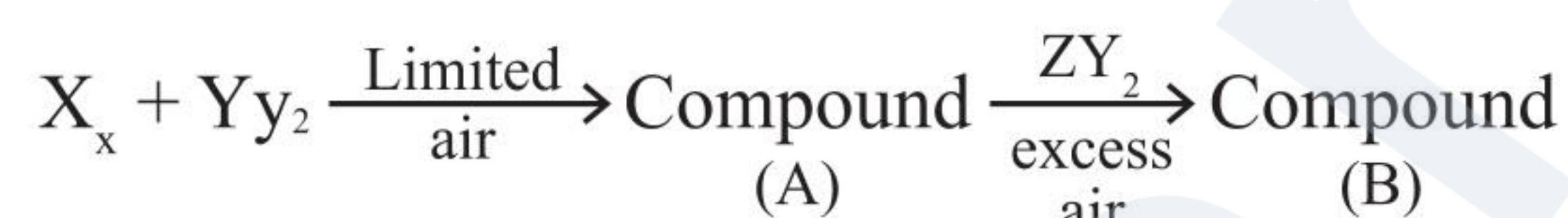
33. Which of the following is incorrect for P_4 molecule of white phosphorus?

- (1) It has 6 lone pairs of electron
 (2) It has 6 P—P single bonds
 (3) It has 3 P—P single bonds
 (4) It has 4 lone pairs of electrons

34. Which of the following statements are incorrect?

- (1) In phosphorous acids, formal oxidation state of P is +1 and +3
 (2) In phosphoric acids, formal oxidation state of P is +5.
 (3) The oxoacids in +3 oxidation state undergo disproportionation reaction to give compounds in lower and higher oxidation states.
 (4) H_3PO_3 is stronger reducing agent than H_3PO_2 .

35. Consider the following reactions:



(Atomic number of element X and Y are 15 and 8)

Select the correct statements :

- (1) (Y—X—Y) bond angle in B > (Y—X—Y) bond angle in A.
 (2) (X—Y) bond length in B < (X—Y) bond length in A.
 (3) Compound A is P_2O_5 and compound B is P_4O_{10}
 (4) Value of $X + Y + Z = 9$

36. Consider the following reactions:

- (i) Hydrolysis of one mole of calcium phosphide
 (ii) Reaction of KOH with 1 mole of white P_4 .

If X is the number of moles of H_2O in reaction (i) and Y is the number of P—H bonds in the products of reaction (ii).

Select the correct statements

- (1) PH_3 is formed in both reactions
 (2) $\text{H}_2\text{PO}_2^\ominus$ is formed in reaction (i)
 (3) The value of Y is 5.
 (4) The value of $X - Y = 1$.

37. What is/are not true about phosphine (PH_3)?

- (1) It turns red litmus blue.
 (2) It reacts with HCl(aq.) to give PH_4Cl
 (3) Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids.
 (4) It is prepared by hydrolysis of metal phosphides with acids.

38. Which of the following reactions can evolve phosphine?

- (1) $\text{White P} + \text{Ca(OH)}_2 \longrightarrow$
 (2) $\text{AlP} + \text{H}_2\text{O} \longrightarrow$
 (3) $\text{H}_3\text{PO}_4 \xrightarrow{\text{Heat}}$
 (4) $\text{PH}_4\text{I} + \text{NaOH} \longrightarrow$

Linked Comprehension Type

Paragraph 1

NH_3 has got pyramidal structure. By replacement of H atoms it forms $(\text{CH}_3)_3\text{N}$ and $(\text{SiH}_3)_3\text{N}$ molecules which are found to have different geometries.

1. Which is the correct relation of bond angles?

- (1) $\text{NH}_3 > (\text{CH}_3)_3\text{N} > (\text{SiH}_3)_3\text{N}$
 (2) $(\text{SiH}_3)_3\text{N} > (\text{CH}_3)_3\text{N} > \text{NH}_3$
 (3) $\text{NH}_3 > (\text{SiH}_3)_3\text{N} > (\text{CH}_3)_3\text{N}$
 (4) $(\text{CH}_3)_3\text{N} > (\text{SiH}_3)_3\text{N} > \text{NH}_3$

2. Shape of $(\text{SiH}_3)_3\text{N}$ with respect to N is

- (1) Pyramidal (2) T-shaped
 (3) Trigonal planar (4) Tetrahedral

3. Which of the following has highest basic character?

- (1) NH_3 (2) $(\text{CH}_3)_2\text{NH}$
 (3) $(\text{CH}_3)_3\text{N}$ (4) $(\text{SiH}_3)_3\text{N}$

Paragraph 2

Solid N_2O_5 exists as $\text{NO}_2^\oplus \text{NO}_3^\ominus$ and hence is called nitronium nitrate.

4. The gas which is acidic in nature is

- (1) NO (2) N_2O
 (3) NO_2 (4) Both (a) and (b)

5. Which of the following statement is correct for the oxides of nitrogen?

- (1) Dinitrogen trioxide dissolves in potassium hydroxide forming potassium nitrate.
 (2) Aqueous solution of nitrogen dioxide behaves both as a reducing agent and as an oxidising agent.
 (3) NO_2 is non-planar.
 (4) Nitrous oxide is fairly soluble in cold water and turns blue litmus red.

6. Choose the incorrect statement:

- (1) NO_2 molecule is angular with N—O distance equal to intermediate distance between a single and a double bond.
 (2) In N_2O_4 the N—N bond length is longer than the usual N—N single bond distance.
 (3) N_2O is a linear molecule and has a small dipole moment.
 (4) None of these

Paragraph 3

PCl_5 has trigonal pyramidal geometry with sp^3d hybridisation in gases and liquid state but in solid state it exists as ionic compound.

7. The hybridisation of P and shape of POCl_3 are

- (1) sp^3 , tetrahedral (2) sp^3d , distorted tetrahedral
(3) sp^3d , square planar (4) sp^3 , pyramidal

8. In presence of small amount of water, PCl_5 hydrolyses to form

- (1) PCl_3 (2) H_3PO_3
(3) POCl_3 (4) POCl

9. In crystalline state PCl_5 exists as

- (1) $[\text{PCl}_3]^{2+} + 2\text{Cl}^-$ (2) $[\text{PCl}_4]^+ [\text{PCl}_6]^-$
(3) $[\text{PCl}_4]^+ \text{Cl}^-$ (4) $[\text{PCl}_6]^+ [\text{PCl}_4]^-$

10. What is the hybridisation state of cation part of solid PCl_5 ?

- (1) sp^3d^2 (2) sp^3d
(3) sp^3 (4) sp^2

Paragraph 4

The pronounced change from non-metallic to metallic behaviour and also increase in the basicity of oxides from nitrogen to bismuth in group 15 is principally due to increasing size of the atoms. The ionisation potential of nitrogen is very high on account of its small size. However, ionisation potential decreases regularly on descending the group.

11. Which one of the following is a strongest base?

- (1) PH_3 (2) SbH_3
(3) AsH_3 (4) NH_3

12. Among the trihalides of nitrogen, which one is least basic?

- (1) NF_3 (2) NI_3
(3) NBr_3 (4) NCl_3

13. Which one of the following fluorides does not exist?

- (1) NF_5 (2) SbF_5
(3) AsF_5 (4) PF_5

14. Which of the following oxides is most acidic?

- (1) Bi_2O_3 (2) P_2O_3
(3) As_2O_3 (4) Sb_2O_3

15. The most unstable hydride is

- (1) NH_3 (2) SbH_3
(3) BiH_3 (4) PH_3

16. In all the group 15 elements, the number of unpaired electrons in the valence shell is

- (1) 2 (2) 3
(3) 4 (4) 5

17. Which trihalide is most ionic among the following?

- (1) NCl_3 (2) PCl_3
(3) BiF_3 (4) SbF_3

Paragraph 5

Phosphorus forms a number of oxoacids which differ in their structures and oxidation state of phosphorus. All the acids contain phosphorus atom/atoms linked tetrahedrally to four

other atoms or groups. Each of them has at least one $\text{P}=\text{O}$ or $\text{P} \rightarrow \text{O}$ unit and one $\text{P}-\text{OH}$ unit. The OH group is ionisable but H atom linked directly to P is non-ionisable. Structures of all the acids are considered to be derived either from phosphorus acid or phosphoric acid.

18. Which one is monobasic acid?

- (1) H_3PO_2 (2) H_3PO_3
(3) H_3PO_4 (4) H_3PO_5

19. Which one has +3 oxidation state?

- (1) H_3PO_4 (2) H_3PO_3
(3) $\text{H}_4\text{P}_2\text{O}_7$ (4) $\text{H}_4\text{P}_2\text{O}_6$

20. The acid which forms two series of salts is

- (1) H_3PO_4 (2) H_3PO_3
(3) HPO_3 (4) H_3PO_2

21. Which of the following is a cyclic oxoacid?

- (1) $\text{H}_4\text{P}_2\text{O}_7$ (2) $\text{H}_4\text{P}_2\text{O}_6$
(3) $\text{H}_4\text{P}_3\text{O}_9$ (4) $\text{H}_5\text{P}_5\text{O}_{15}$

22. The number of $\text{P}=\text{O}$ and $\text{P}-\text{O}-\text{H}$ bonds in H_3PO_4 are

- (1) 3, 1 (2) 2, 2
(3) 1, 2 (4) 1, 3

Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column—II.

1.	Column I		Column II
(1)	Superphosphate of lime	p.	N_2O
(2)	Laughing gas	q.	N_2
(3)	Inert gas	r.	NH_4Cl
(4)	Sal ammoniac	s.	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

2.	Column I		Column II
(1)	Anhydride of HNO_3	p.	Phosphorous trioxide
(2)	Anhydride of HNO_2	q.	Phosphorous pentoxide
(3)	Anhydride of HPO_3	r.	Nitrogen pentoxide
(4)	Anhydride of H_3PO_3	s.	Nitrogen trioxide

3.	Mixture		Solution used for separation
(1)	PH_3 and NH_3	p.	H_2SO_4
(2)	N_2 and NH_3	q.	Ammoniacal CuCl
(3)	N_2 and Co	r.	Water
(4)	N_2 and O_2	s.	Pyrogallol

4.	Column I		Column II
(1)	Dibasic acid	p.	Phosphorous acid
(2)	Tribasic acid	q.	Ammonium nitrate
(3)	Monobasic acid	r.	Orthophosphoric acid
(4)	Freezing salt	s.	Hypophosphorous acid

5.

	Column I		Column II
(1)	Acid hydride of N	p.	Nitrogen dioxide
(2)	Basic hydride of N	q.	Ammonia
(3)	Brown coloured gas	r.	Hydrazoic acid
(4)	Colourless gas	s.	Nitric oxide

6.

	Column I		Column II
(1)	Salammoniac	p.	Ammonia
(2)	Haber process	q.	Ammonium chloride
(3)	Ostwald's process	r.	$\text{NH}_4\text{NO}_3 + \text{CaCO}_3$
(4)	Nitrochalk	s.	Nitric acid

7.

	Column I		Column II
(1)	Hypophosphorous acid	p.	$\text{H}_4\text{P}_2\text{O}_7$
(2)	Phosphorous acid	q.	H_3PO_4
(3)	Phosphoric acid	r.	H_3PO_3
(4)	Pyrophosphoric acid	s.	H_3PO_2

8.

	Column I (Reactions)		Column II (Products)
(1)	Hg and Pb with dil HNO_3	p.	Metal nitrates + H_2

(2)	Zn, Fe and Sn with very dil. HNO_3	q.	Metal nitrates + NH_2OH or NH_4NO_3
(3)	Zn, Fe and Sn with dil. HNO_3	r.	Metal nitrates + NO
(4)	Mg, Mn and Ca with dil. HNO_3	s.	Metal nitrates + N_2O

9.

	Column I (Reactions)		Column II (Products)
(1)	Cu, Ag, Hg, Pb and Zn with conc. HNO_3	p.	H_2SnO_3 and NO_2
(2)	Fe with moderately conc. HNO_3	q.	Metal nitrates + NO_2
(3)	Fe, Al, Co, Ni and Cr with conc. HNO_3	r.	Ferric nitrate + NO_2
(4)	Sn with conc. HNO_3	s.	Rendered passive

10.

	Column I		Column II
(1)	Phosphorite	p.	$3\text{Ca}_3(\text{PO}_4)_2\text{CaCl}_2$
(2)	Chloroapatite	q.	$3\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$
(3)	Fluoroapatite	r.	CAN
(4)	Nitrochalk	s.	$\text{Ca}_3(\text{PO}_4)_2$

11. Match the items given in Column I with that in Column II and III

	Column I		Column II		Column III
	Oxides of nitrogen		Method of preparation		Characteristics
(1)	N_2O	i.	$\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + \text{O}_2 + \dots\dots$ LiNO_3 and $\text{Mg}(\text{NO}_3)_2$, also give same reaction.	p.	Colourless, neutral gas. On heating at 600°C , gives $\text{N}_2 + \text{O}_2$
(2)	NO	ii.	$4\text{AgNO}_3 + 2\text{Cl}_2 \longrightarrow 4\text{AgCl} + \text{O}_2 + \dots\dots\dots$	q.	Colourless gas, in solid and liquid state it is blue in colour. On heating at 1100°C , gives $\text{N}_2 + \text{O}_2$
(3)	NO_2	iii.	$\text{NH}_4\text{NO}_3 \xrightarrow{250^\circ\text{C}} \dots\dots\dots + 2\text{H}_2\text{O}$	r.	It is an hydride of HNO_3 and acidic in nature. In solid state, it exists as: $[\text{NO}_2]^\oplus [\text{NO}_3]^\ominus$
(4)	N_2O_5	iv.	Catalytic oxidation of NH_3 . $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} \dots\dots\dots + 6\text{H}_2\text{O}$	s.	Brown gas highly reactive and paramagnetic Acts as an oxidising agent.

12. Match the items given in Column I with that in Column II and III

	Column I		Column II		Column III
	Different concentration of HNO_3		Elements		Main products
(1)	Conc. HNO_3	i.	Fe, Al, CO, Ni, and Cr	p.	Complex ions + NO(g)
(2)	Dil. HNO_3	ii.	Cu, Ag, Hg, Pb and Zn	q.	Rendered passive
(3)	Cold dil. HNO_3	iii.	Noble metals like Au, Pt	r.	Metal nitrates + NO(g)
(4)	Aqua regia	iv.	Cu, Ag, Hg and Pb	s.	Metal nitrates + NO_2 (g)
		v.	Mg and Mn	t.	Metal nitrates + H_2 (g)

For Q. 13 to Q. 16:

Answer the questions given below by appropriately matching the information given in three Column of the following table.

	E.C. of 15 group elements		Characteristics (I)		Characteristics (II)
(1)	$6s^2 6p^3$	i.	Metalloid	p.	Least stable hydride.
(2)	$3s^2 3p^3$	ii.	Basic oxides and metallic in character	q.	Exists in tetrahedral tetra-atomic forms and are solid
(3)	$4s^2 4p^3$	iii.	Its hydride have highest bond angle amongst other hydrides	r.	Do not form sulphides
(4)	$2s^2 2p^3$	iv.	Graham salt	s.	Shows inert pair effect

13. For the element nitrogen, CORRECT combination is:

- (1) b—iv—q (2) b—iv—q,s
(3) d—iii—r (4) d—iv—q,s

14. For the element phosphorous, CORRECT combination is:

- (1) b—iv—q (2) b—iv—q,s
(3) d—iii—r (4) d—iv—q,s

15. For the element arsenic, CORRECT combination is:

- (1) b—iv—q,s (2) b—iv—s
(3) c—i—q (4) c—i—q,s

16. For the element bismuth, CORRECT combination is:

- (1) a—ii—p,q,s (2) a—ii—p,q
(3) a—ii—p (4) a—i—p,q,s

Numerical Value Type

- How many nitrogen oxides are known?
- How many lone pairs are present in nitrogen molecule?
- In group 15 elements, the number of unpaired electrons in valence shell is _____.
- How many P—O—P bonds are present in P_4O_8 ?
- In solid PCl_5 molecule, how many P—Cl bonds are present in the cation?
- What is the basicity of pyrophosphoric acid?

- How many σ -bonds are present in N_2O_3 ?
- When excess of ammonia and chlorine react, nitrogen and ammonium chloride are formed. Write the balanced equation and find out how many ammonium chloride molecules are involved in the balanced equation?
- What is the atomicity of phosphorous?
- How many N—O (σ) bonds are present in N_2O_5 ?
- In P_4O_{10} , how many oxygen atoms are bonded to each phosphorous atoms?
- How many unpaired electrons are present in NO molecule?
- The number of vacant orbitals in the valence shell of phosphorous is _____.
- How many hydrogen bonds are formed by each H_3PO_4 molecule?
- On hydrolysis, of calcium phosphide, how many moles of phosphine are formed?
- How many lone pairs are present in white phosphorous?
- How many bridging oxygen atoms are present in P_4O_{10} ?
- How many moles of H_3PO_4 are obtained on hydrolysis of one mole of P_4O_8 .
- On hydrolysis of magnesium nitride, how many moles of ammonia are produced?
- How many electrons are present in the valence shell of P in PCl_3 ?
- The following oxides of nitrogen are given:
(i) N_2O (ii) NO (iii) N_2O_3
(iv) NO_2 (v) N_2O_4 (vi) N_2O_5
If X is the number of neutral oxide and Y is the number of paramagnetic oxide then find the value of $\frac{(X+Y)^2}{5}$.

22. In the following compounds

- (i) P_4O_{10} (ii) Solid PI_5

Calculate the value of $\left(\frac{X+Y}{6}\right)$.

If X is the total number of sp^3 hybridised atoms in both above compounds Y is the total number of sp^2 hybridised atoms in both above compounds.

Archives

JEE ADVANCED

Single Correct Answer Type

- The reaction of P with X leads selectively to P_4O_6 . X is
(1) dry O_2
(2) a mixture of O_2 and N_2
(3) moist O_2
(4) O_2 in the presence of aqueous NaOH (IIT-JEE 2009)
- Extra pure N_2 can be obtained by heating
(1) NH_3 with CuO (2) NH_4NO_3
(3) $(NH_4)_2Cr_2O_7$ (4) $Ba(N_3)_2$
(IIT-JEE 2011)

- The reaction of white phosphorous with aqueous NaOH gives phosphine along with another phosphorous containing compound. The reaction type; the oxidation state of phosphorous in phosphine and in the other products are, respectively,
(1) redox reaction; -3 and -5
(2) redox reaction; +3 and +5
(3) disproportionation reaction; -3 and +5
(4) disproportionation reaction; -3 and +3 (IIT-JEE 2012)
- Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?

- (1) HNO_3 , NO , NH_4Cl , N_2 (2) HNO_3 , NO , N_2 , NH_4Cl
 (3) HNO_3 , NH_4Cl , NO , N_2 (4) NO , HNO_3 , NH_4Cl , N_2

(IIT-JEE 2012)

5. The product formed in the reaction of SOCl_2 (thionyl chloride) with white phosphorous is

- (1) PCl_3 (2) SO_2Cl_2
 (3) SCl_2 (4) POCl_3

(JEE Advanced 2014)

6. The order of the oxidation state of the phosphorus atom in H_3PO_2 , H_3PO_4 , H_3PO_3 and $\text{H}_4\text{P}_2\text{O}_6$ is

- (1) $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
 (2) $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$
 (3) $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$
 (4) $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$

(JEE Advanced 2017)

Multiple Correct Answers Type

1. The nitrogen oxide(s) that contains N—N bond is/are

- (1) N_2O (2) N_2O_3
 (3) N_2O_4 (4) N_2O_5 (IIT-JEE 2010)

2. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}

- (1) can also be prepared by reaction of P_4 and HNO_3
 (2) is diamagnetic
 (3) contains one N—N bond
 (4) react with Na metal producing a brown gas

(JEE Advanced 2016)

3. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)

- (1) NH_4NO_3 (2) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
 (3) $\text{Ba}(\text{N}_3)_2$ (4) Mg_3N_2

(JEE Advanced 2018)

4. Based on the compounds of group 15 elements, the correct statement(s) is (are)

- (1) Bi_2O_5 is more basic than N_2O_5
 (2) NF_3 is more covalent than BiF_3
 (3) PH_3 boils at lower temperature than NH_3
 (4) N—N single bond is stronger than the P—P single bond

(JEE Advanced 2018)

5. The correct statement(s) related to oxoacids of phosphorous is(are)

- (1) Upon heating, H_3PO_3 undergoes disproportionation reaction to produce H_3PO_4 and PH_3 .
 (2) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.
 (3) H_3PO_3 is a monobasic acid.
 (4) The H atom of P—H bond in H_3PO_3 is not ionizable in water.

(JEE Advanced 2021)

Linked Comprehension Type

Paragraph 1

There are some deposits of nitrates and phosphates in the earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under laboratory conditions but microbes do it easily. Ammonia forms a large number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of NH_3 and PH_3 . Phosphine is a flammable gas and is prepared from white phosphorus.

1. Which of the following statements is correct?

- (1) Phosphates have no biological significance in humans.
 (2) Between nitrates and phosphates, phosphates are less abundant in earth's crust.
 (3) Between nitrates and phosphates, nitrates are less abundant in earth's crust.
 (4) Oxidation of nitrates is possible in soil.

2. Which of the following statements is correct?

- (1) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.
 (2) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies sp^2 -orbital and is more directional.
 (3) Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 -orbital and is more directional.
 (4) Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.

3. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a

- (1) dimerisation reaction
 (2) disproportionation reaction
 (3) condensation reaction
 (4) precipitation reaction

(IIT-JEE 2008)

Paragraph 2

Upon heating KClO_3 in the presence of catalytic amount of MnO_2 , a gas W is formed. Excess amount of W reacts with white phosphorus to give X . The reaction of X with pure HNO_3 gives Y and Z .

4. W and X are, respectively

- (1) O_3 and P_4O_6 (2) O_2 and P_4O_{10}
 (3) O_3 and P_4O_{10} (4) O_2 and P_4O_6

5. Y and Z are, respectively

- (1) N_2O_4 and H_3PO_3 (2) N_2O_4 and HPO_3
 (3) N_2O_5 and HPO_3 (4) N_2O_3 and H_3PO_4

(JEE Advanced 2017)

Matrix Match Type

1. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

	Column I		Column II
(a)	$\text{Cu} + \text{dil HNO}_3$	p.	NO
(b)	$\text{Cu} + \text{conc HNO}_3$	q.	NO_2
(c)	$\text{Zn} + \text{dil HNO}_3$	r.	N_2O
(d)	$\text{Zn} + \text{conc HNO}_3$	s.	$\text{Cu}(\text{NO}_3)_2$
		t.	$\text{Zn}(\text{NO}_3)_2$

Numerical Value Type

1. What is the total number of diprotic acids among the following?
 H_3PO_4 , H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_3BO_3 , H_3PO_2 , H_2CrO_4 , H_2SO_3
(IIT-JEE 2010)
2. Among the following, the number of compounds that can react with PCl_5 to give POCl_3 is
 O_2 , CO_2 , SO_2 , H_2O , H_2SO_4 , P_4O_{10}
(IIT-JEE 2011)
3. The total number of compounds having at least one bridging oxo group among the molecules given below is _____.
 N_2O_3 , N_2O_5 , P_4O_6 , P_4O_7 , $\text{H}_4\text{P}_2\text{O}_5$, $\text{H}_5\text{P}_3\text{O}_{10}$, $\text{H}_2\text{S}_2\text{O}_3$, $\text{H}_2\text{S}_2\text{O}_5$
(JEE Advanced 2018)

Answers Key**EXERCISES****Single Correct Answer Type**

- | | | | | |
|----------|----------|----------|----------|----------|
| 1. (1) | 2. (2) | 3. (3) | 4. (2) | 5. (4) |
| 6. (2) | 7. (1) | 8. (2) | 9. (2) | 10. (1) |
| 11. (4) | 12. (2) | 13. (2) | 14. (1) | 15. (1) |
| 16. (2) | 17. (2) | 18. (4) | 19. (4) | 20. (1) |
| 21. (1) | 22. (1) | 23. (4) | 24. (1) | 25. (2) |
| 26. (1) | 27. (1) | 28. (1) | 29. (3) | 30. (4) |
| 31. (2) | 32. (2) | 33. (3) | 34. (4) | 35. (4) |
| 36. (3) | 37. (2) | 38. (2) | 39. (4) | 40. (1) |
| 41. (1) | 42. (2) | 43. (2) | 44. (2) | 45. (1) |
| 46. (3) | 47. (3) | 48. (1) | 49. (3) | 50. (1) |
| 51. (3) | 52. (1) | 53. (4) | 54. (1) | 55. (2) |
| 56. (2) | 57. (1) | 58. (3) | 59. (2) | 60. (3) |
| 61. (4) | 62. (3) | 63. (3) | 64. (4) | 65. (2) |
| 66. (3) | 67. (3) | 68. (3) | 69. (4) | 70. (3) |
| 71. (3) | 72. (3) | 73. (3) | 74. (3) | 75. (2) |
| 76. (1) | 77. (1) | 78. (4) | 79. (1) | 80. (1) |
| 81. (3) | 82. (3) | 83. (1) | 84. (1) | 85. (4) |
| 86. (1) | 87. (2) | 88. (2) | 89. (1) | 90. (1) |
| 91. (3) | 92. (2) | 93. (4) | 94. (4) | 95. (3) |
| 96. (1) | 97. (1) | 98. (1) | 99. (1) | 100. (4) |
| 101. (1) | 102. (1) | 103. (2) | 104. (4) | 105. (1) |
| 106. (1) | 107. (2) | 108. (2) | 109. (2) | 110. (1) |
| 111. (2) | 112. (4) | 113. (1) | 114. (4) | 115. (1) |
| 116. (3) | 117. (3) | | | |

Multiple Correct Answers Type

- | | | | | |
|------------------|------------------|---------------|---------------|------------|
| 1. (1, 2, 4) | 2. (1, 2, 4) | 3. (1, 2, 4) | 4. (1, 2) | 5. (1, 4) |
| 6. (2, 4) | 7. (3, 4) | 8. (1, 2) | 9. (1, 2, 3) | 10. (3, 4) |
| 11. (2, 3, 4) | 12. (1, 2, 3, 4) | 13. (1, 2, 3) | 14. (1, 3, 4) | 15. (1, 3) |
| 16. (1, 2, 3, 4) | 17. (1, 2, 4) | 18. (2, 3) | 19. (1, 2, 3) | 20. (1, 2) |
| 21. (1, 2, 3) | 22. (1, 2, 3) | 23. (1, 3) | 24. (2, 3) | 25. (3, 4) |
| 26. (3, 4) | 27. (2, 3, 4) | 28. (2, 3) | 29. (1, 2) | 30. (2, 3) |

31. (2, 3) 32. (2, 4) 33. (1, 3) 34. (4) 35. (1, 2, 4)
 36. (1, 3, 4) 37. (1, 2) 38. (1, 2, 3)

Linked Comprehension Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (2) | 2. (3) | 3. (3) | 4. (3) | 5. (2) |
| 6. (4) | 7. (1) | 8. (3) | 9. (2) | 10. (3) |
| 11. (4) | 12. (1) | 13. (1) | 14. (2) | 15. (3) |
| 16. (2) | 17. (3) | 18. (1) | 19. (2) | 20. (3) |
| 21. (3) | 22. (4) | | | |

Matrix Match Type

Q. No.	(a)	(b)	(c)	(d)
1.	s	p	q	r
2.	r	s	q	p
3.	r	p	q	s
4.	p	r	s	q
5.	r	q	p	s
6.	q	p	s	r
7.	s	r	q	p
8.	r	q	s	p
9.	q	r	s	p
10.	s	p	q	r
11.	iii-p	iv-q	i-s	ii-r
12.	i, ii-q,s	iv-r,	v-t,	iii-p

13. (3) 14. (2) 15. (4) 16. (1)

Numerical Value Type

- | | | | | |
|-----------|-----------|---------|---------|---------|
| 1. (5) | 2. (2) | 3. (3) | 4. (6) | 5. (4) |
| 6. (4) | 7. (4) | 8. (6) | 9. (4) | 10. (6) |
| 11. (4) | 12. (1) | 13. (5) | 14. (4) | 15. (2) |
| 16. (4) | 17. (6) | 18. (2) | 19. (2) | 20. (8) |
| 21. (3.2) | 22. (2.5) | | | |

ARCHIVES**JEE Advanced****Single Correct Answer Type**

1. (2) 2. (4) 3. (3) 4. (2) 5. (1)
6. (1)

Multiple Correct Answers Type

1. (1, 2, 3) 2. (2, 4) 3. (2, 3) 4. (1, 2, 3)
5. (1, 2, 4)

Linked Comprehension Type

1. (3) 2. (3) 3. (2) 4. (2) 5. (2)

Matrix Match Type

1. (a) p, s (b) q, s (c) r, t (d) q, t

Numerical Value Type

1. (6) 2. (4) 3. (6)

Chapter 2

Concept Application Exercises

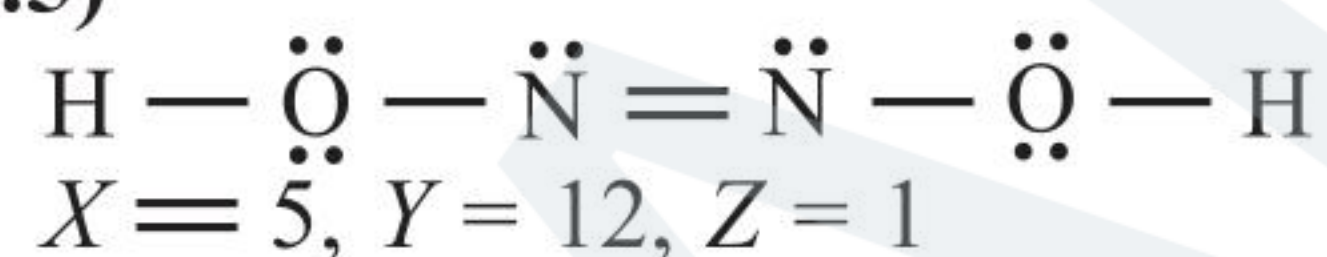
Exercise 2.1

1. (a) $\text{P}_4(\text{Red}) + 6\text{I}_2 \longrightarrow 4\text{PI}_3$
 $2\text{PI}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HI}$
- (b) $\text{P}_4 + 3\text{NaOH} + \text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_2 + 4\text{PH}_3$
 White Sodium hypophosphite Phosphine
- (c) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$
- (d) $\text{I}_2 + 10\text{HNO}_3(\text{conc.}) \longrightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$
- (e) $\text{H}_3\text{PO}_4 + 21\text{HNO}_3 + 12(\text{NH}_4)_2\text{MoO}_4 \longrightarrow$
 $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 + 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$
- (f) $\text{Na}_2\text{HPO}_4 + \text{MgSO}_4 + \text{NH}_4\text{OH} \longrightarrow \text{MgNH}_4\text{PO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
- (g) $3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
 $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$
- (h) $\text{PH}_3 + 3\text{AgNO}_3 \longrightarrow \text{Ag}_3\text{P} + 3\text{HNO}_3$
- (i) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[\Delta]{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$
- (j) $2\text{Au} + 3\text{HNO}_3 + 11\text{HCl} \longrightarrow 2\text{HAuCl}_4 + 3\text{NOCl} + 6\text{H}_2\text{O}$
- (k) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
- (l) $2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \longrightarrow \text{P}_4 + 10\text{CO} + 6\text{CaSiO}_3$
- (m) $\text{P}_4 + 10\text{HNO}_3 + \text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{PO}_4 + 5\text{NO} + 5\text{NO}_2$
- (n) $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
- (o) $\text{PH}_3 + 3\text{CuSO}_4 \longrightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$

2. (a) $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
- (b) $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$
- (c) $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$
- (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
- (e) $2\text{H}_3\text{PO}_3 \xrightarrow{\Delta} \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$
- (f) $4\text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3\text{H}_3\text{PO}_4 + \text{PH}_3$
- (g) $2\text{H}_3\text{PO}_2 \xrightarrow{\Delta} \text{H}_3\text{PO}_4 + \text{PH}_3$
- (h) $2\text{Cu}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{CuO} + 2\text{NO}_2 + \text{O}_2$

3. i. $\text{P}_4\text{O}_{10} + 6\text{PCl}_5 \longrightarrow 10\text{POCl}_3$
- ii. $2\text{NH}_3 + \text{NaOCl} \longrightarrow \text{NH}_2\text{NH}_2 + \text{NaCl} + \text{H}_2\text{O}$
- iii. $\text{Ca}_3(\text{PO}_4)_2 + \text{H}_3\text{PO}_4 \longrightarrow 3\text{Ca}(\text{H}_2\text{PO}_4)_2$
- iv. $\text{AgCl} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$
- v. $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$
- vi. $\text{Mg} + 2\text{HNO}_3 \longrightarrow \text{Mg}(\text{NO}_3)_2 + \text{H}_2$

4. (16.5)



$$X = 5, Y = 12, Z = 1$$

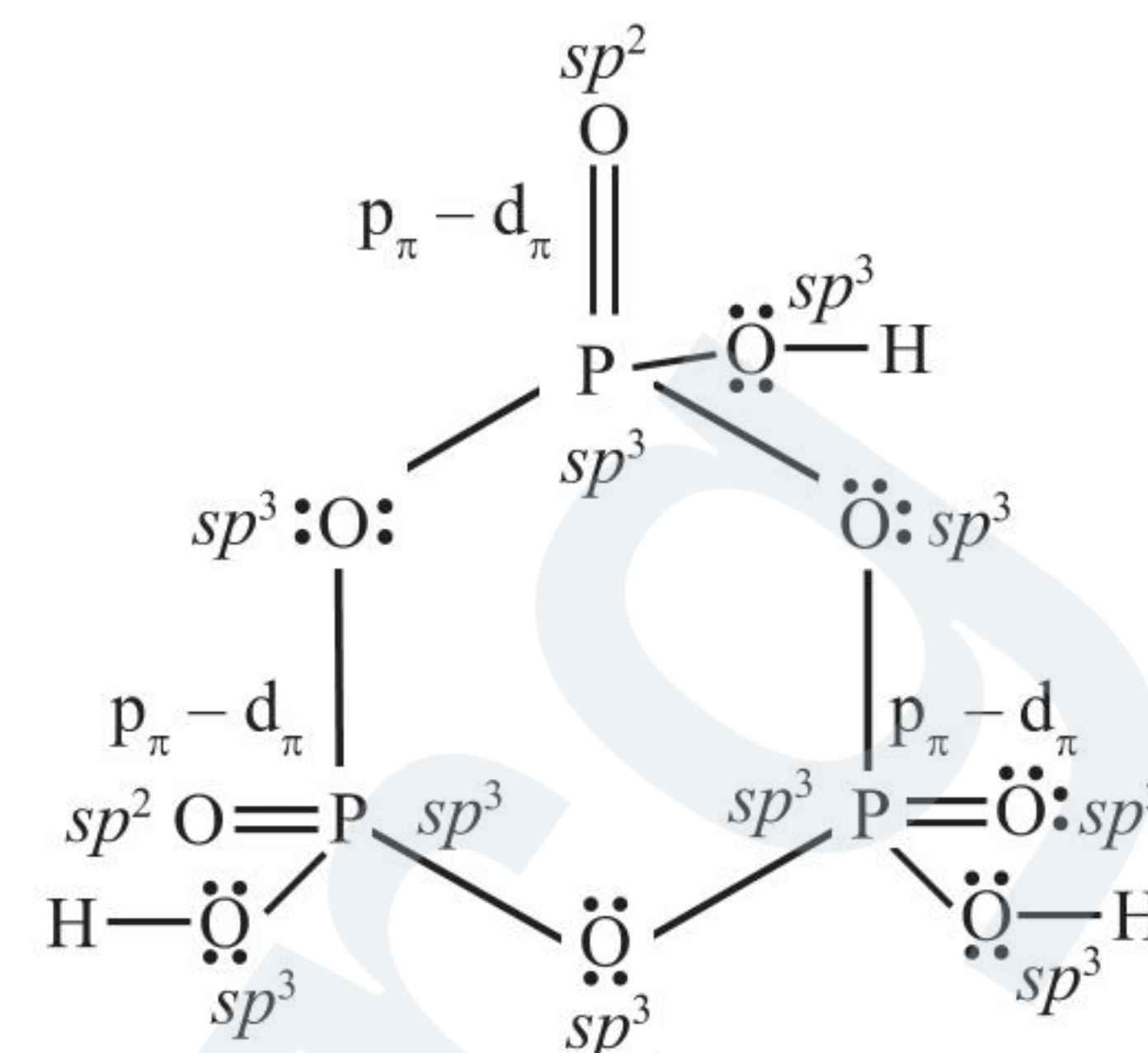
$$\therefore \left(X + Y - \frac{Z}{2} \right) = \left(5 + 12 - \frac{1}{2} \right) = 16.5$$

5. (1.8)

- (i) $\text{PO}_3^\ominus$ (metaphosphate ion)
 O.S of P = +5 = X
- (ii) $\text{H}_2\text{PO}_2^\ominus$ (Dihydrogen hypophosphite ion)
 O.S of P = +1 = Y
- (iii) $\text{H}_2\text{PO}_3^\ominus$ (Dihydrogen phosphite ion).
 O.S of P = +3 = Z.

$$\therefore \frac{X + Y + Z}{5} = \frac{5 + 1 + 3}{5} = 1.8$$

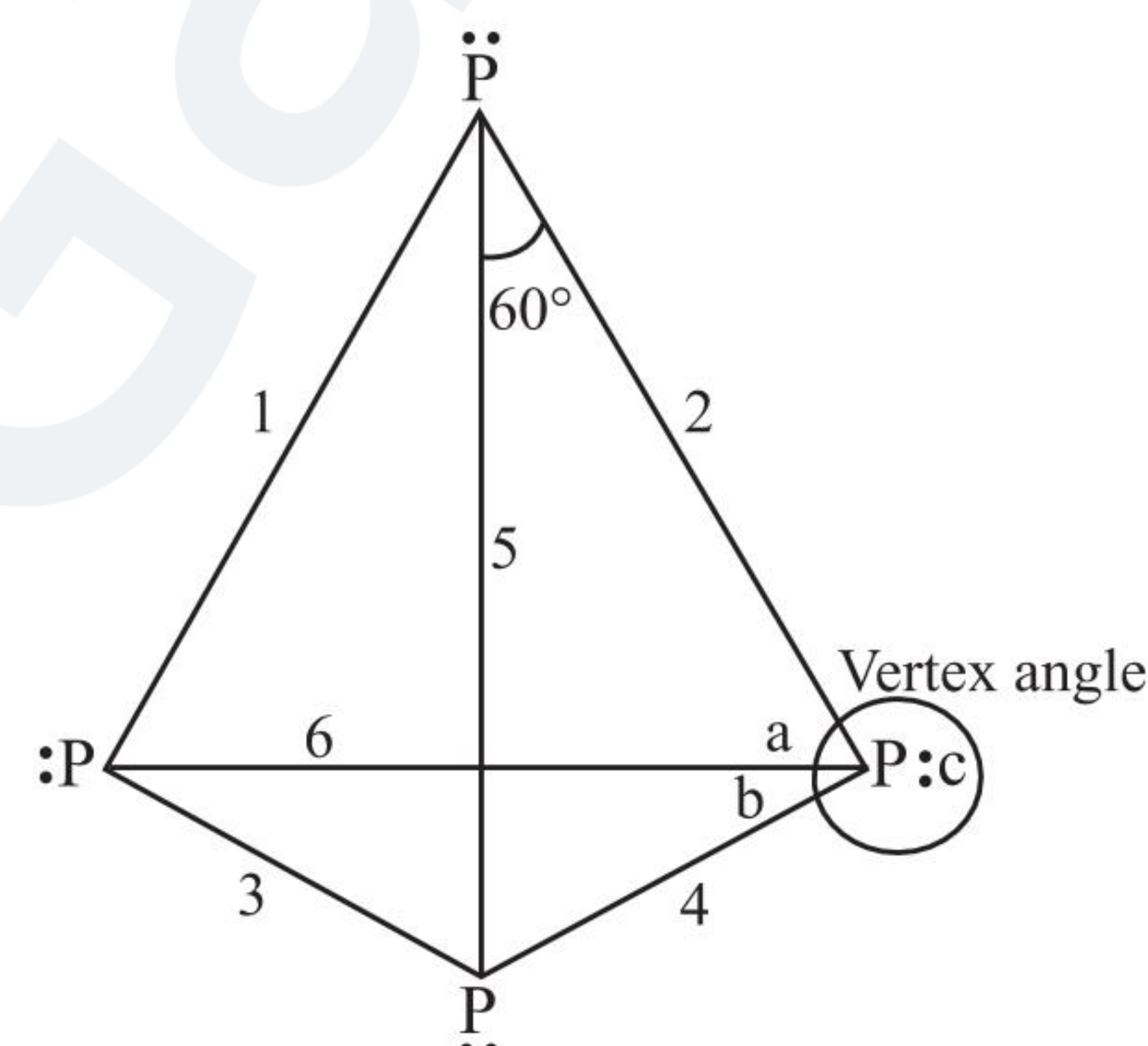
6. (2.25)



$$X = 3, Y = 9, Z = 3$$

$$\therefore \frac{X + Y - Z}{4} = \frac{3 + 9 - 3}{4} = 2.25$$

7. (5.2)



Phosphorous exists as P_4 molecule.

P = Atomicity = 4

Total vertex angle : 3 angle (a, b, and c) on each P atoms.

$$\therefore Q = 3 \times 4 = 12$$

R = (P—P) bond = 6

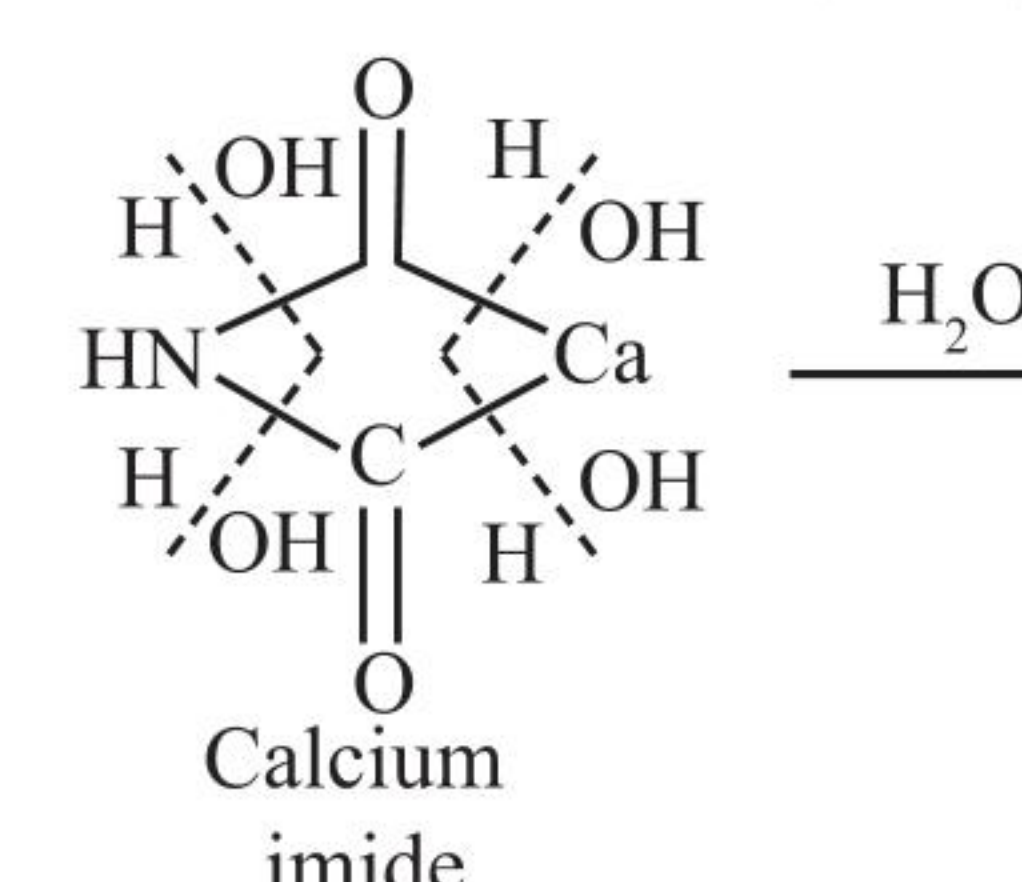
S = Lone pairs = 4.

$$\therefore \frac{P + Q + R + S}{5} = \frac{4 + 12 + 6 + 4}{5} = 5.2$$

Exercises

Single Correct Answer Type

1. (1) Correct (1) single N—N bond is weaker than P—P bond. That is why P shows allotropy but N does not.
- (2) PH_3 acts as ligands due to lp e^- s.
- (3) NO_2 is paramagnetic due to one unpaired e^- s.
- (4) True
2. (2) The reducing character of 15 group hydrides increases down the group due to increase in thermal stability from NH_3 to BiH_3 .
3. (3) B. Pt order:
 $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
 290 254.6 238.5 210 85.5 K
4. (2) Due to inert pair effect stability of +3 O.S increases down the group BiF_5 exists due to small size and high electronegativity of F-atom.
5. (4) In solid state PCl_5 exists as.
 $[\text{PCl}_4]^\oplus$ $[\text{PCl}_6]^\ominus$
 sp^3 sp^3d^2
 Tetrahedral Octahedral
6. (2) B.Pt. increases down the group due to increase in their size. (except P < N.)

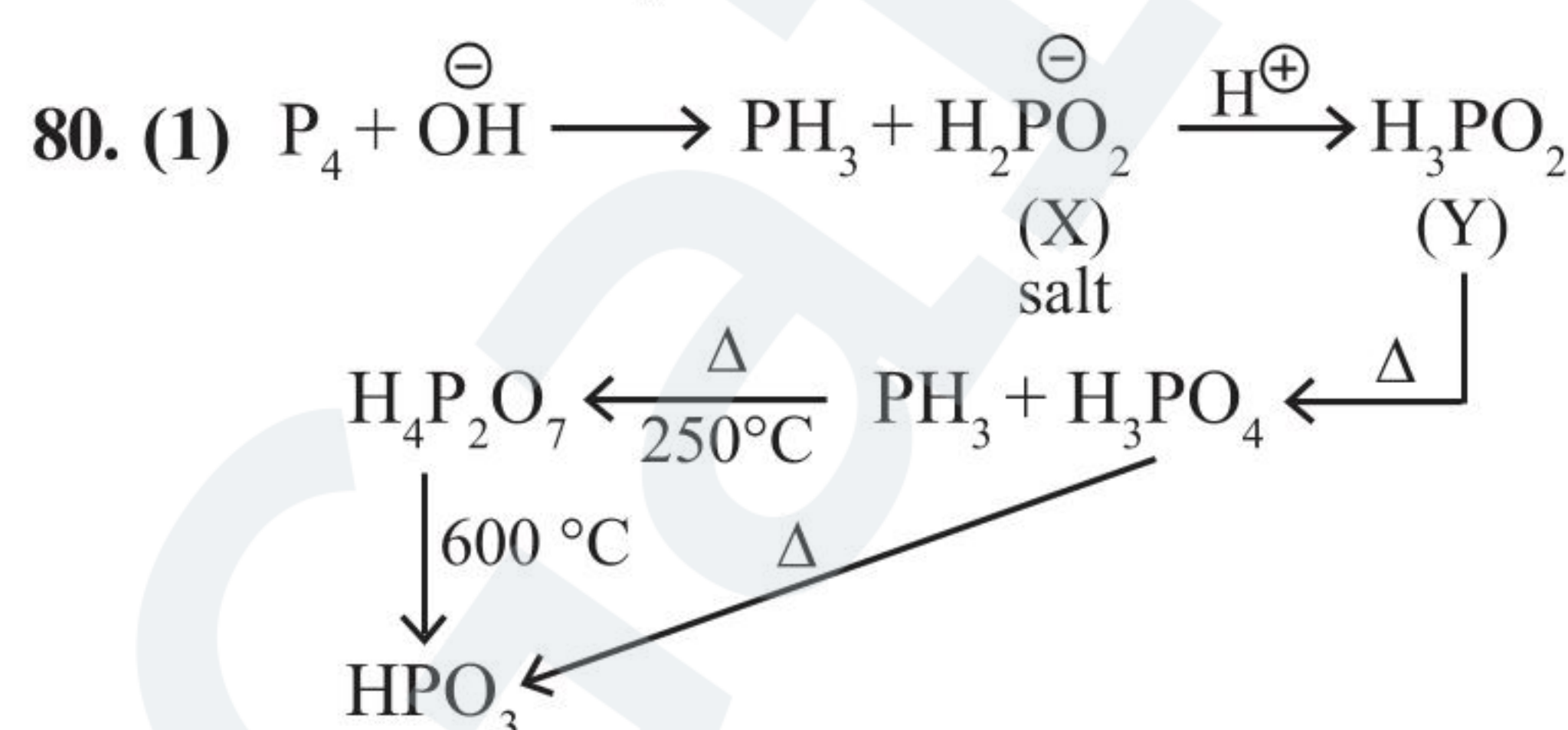
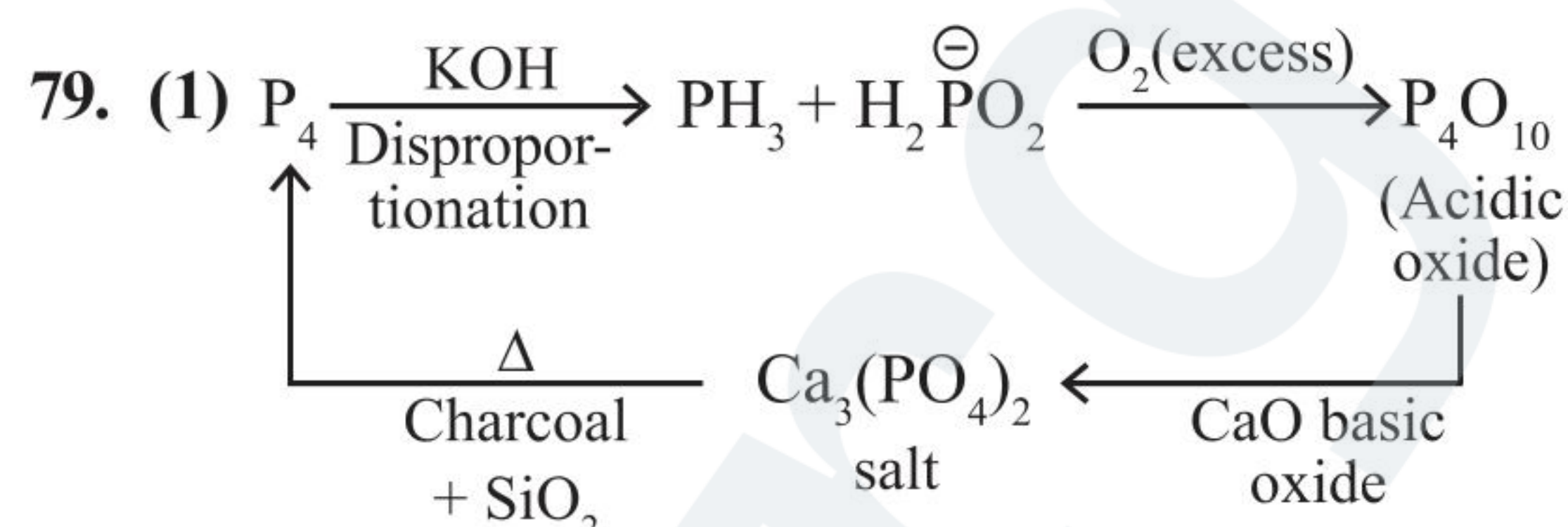
7. (1) Thermal stability decreases down the group due to increase in bond length (M—H) down the group and bond strength (M—H) decreases down the group.
8. (2) Factual
9. (2) Refer to structure of P_4O_{10} .
 $(P—O—P)$ bond = 6 = X
 PI_5 exists as:
 $[PI_4]^+ [I]^-$
 $(P—I)$ bond = 4 = Y
 $\therefore X - Y = 6 - 4 = 2$
10. (1)
11. (4)
12. (2) P_4 exists as tetrahedra tetraatomic discrete molecule with P—P—P bond angle of 60° , hence atomicity of P = 4.
13. (2)
14. (1)
15. (1) Hyponitrous acid
 $(H_2N_2O_2)$ $(HO—\ddot{N}=\ddot{N}—OH)$ contains one $(p\pi - p\pi)$ bond
16. (2) Active nitrogen is prepared by passing electric spark through N_2 gas at 2 mm pressure. This is called atomic nitrogen which reacts with acetylene.
 $HC\equiv CH + 2N \longrightarrow C_2N_2 + H_2$
(cyanogen)
17. (2) N_2O is a colourless gas.
18. (4) $N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$
19. (4) Factual
20. (1) Factual
21. (1) Factual
22. (1)
(i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
(Black) (greenish yellow gas)
- (ii) $3Cl_2 + NH_3 \xrightarrow{-3} NCl_3 + 3HCl$
23. (4) $2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$
24. (1) $NH_4Cl + NaNO_3 \xrightarrow{\Delta} N_2O + NaCl + 3H_2O$
25. (2) $NO + NO_2 \xrightarrow{\Delta} N_2O_3$
26. (1)
(a) (F) As the size of halogen atoms increases, crowding on Si atom will increase, hence tendency of attack of Lewis base decreases.
(b) (T) M.Pt. of NH_3 is higher due to H-bonding.
(c) (F) M.Pt. and B.Pt increases from PH_3 to SbH_3 due to increase in molecular mass, but NH_3 is exception (due to H-bonding)
B.Pt. order :
 $SbH_3 > NH_3 > AsH_3 > PH_3$
(d) (T)
27. (1) $(NH_4)_2Cr_2O_7$ (X) $\xrightarrow{\text{Heat}}$ Cr_2O_3 + $N_2 + 4H_2O$
Amm.dichromate (orange solid) Chromic oxides (Green residue) (Colourless gass) (Y)
- $N_2 + Mg \longrightarrow Mg_3N_2$
(Y) (white)
28. 1.

Calcium imide + $H_2O \longrightarrow NH_3$ (B) + $[HCOOH] + Ca(OH)_2$
2. $2NH_3 + 3CaOCl_2 \longrightarrow 3CaCl_2 + 3H_2O + N_2$
(B) Bleaching powder (C)
3. $N_2 + 3Mg \longrightarrow Mg_3N_2 \xrightarrow{6H_2O} 3Mg(OH)_2 + 2NH_3$
(C) Magnesium nitride (D) (B)
29. (3) (a) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
(b) $NH_4Cl + NaNO_2 \longrightarrow NH_4NO_2 \xrightarrow[\Delta]{+NaCl} N_2(g) + 2H_2O$
(c) $NH_4Cl + CaO \longrightarrow CaCl_2 + 2NH_3 + H_2O$
(It does not give N_2 but gives NH_3)
(d) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$
30. (4) $NH_2OH + HNO_2 \xrightarrow{\Delta} N_2O + 2H_2O$
31. (2) Factual
32. (2) In NCl_3 , H_2O attacks on less Electronegative Cl-atom than central N-atom.
 $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$
33. (3) Reducing character $\propto \frac{1}{(M-H) \text{ bond energy}}$
Correct (3): $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
34. (4)
35. (4) NH_3 is a weak reducing agent than PH_3 , because X—H bond strength decreases down the group.
Due to absence of H-bond only weak van der Waals force of attraction exists in PH_3 , Hence it has lower critical temperature than NH_3 .
36. (3) Due to resonance in N_2O_4 , N—N bond length (186 pm) is smaller than (N—N) bond length in $(H_2N—NH_2)$.
37. (2) (1) $2NaNO_3 \xrightarrow{500^\circ C} 2NaNO_2 + O_2$
 $4NaNO_3 \xrightarrow{800^\circ C} 2Na_2O + 5O_2 + 2N_2$
(2) $AgNO_3 \xrightarrow{\Delta} Ag + \frac{1}{2} O_2 + NO_2$
(3) $NH_4NO_3 \xrightarrow[250^\circ C]{\Delta} N_2O + 2H_2O$
(4) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$
38. (2)
 $I_2 \longrightarrow IO_3^-$, $NO_3^- \longrightarrow NO_2$
 $I_2 + 10NO_3^- + 8H^+ \longrightarrow 2IO_3^- + 10NO_2 + 4H_2O$
39. (4) (a) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$
(b) $2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$
(c) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3(s) + 4H_2O$
green
40. (1) $NO + NO_2 \xrightarrow{243K} N_2O_3 \xrightarrow{H_2O} HNO_2$
(X) (Y)
Blue Coloured Solid
 NO_2^- is sp^2 -hybridised, and triangular planar in shape.
41. (1) $Na + NH_3 \xrightarrow{\Delta} NaNH_2 + \frac{1}{2} H_2$
(X)
 $\downarrow N_2O$
 $N_2 \xleftarrow{\Delta} NaN_3$
(Z) (Y)
42. (2) Factual

43. (2) $\text{HNO}_2 + \text{HNO}_3 \longrightarrow \text{NO}_2 + \text{H}_2\text{O}$
Hence NO_2 is mixed anhydride of HNO_2 and HNO_3 .
44. (2) $3\text{Cu} + 8\text{HNO}_3(\text{dil}) \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
45. (1)
46. (3) $2\text{AgNO}_3 \xrightarrow{\Delta} 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$
47. (3)
48. (1)
49. (3) $\text{N}_2 + \text{Ca} + \text{C} \longrightarrow \text{CaCN}_2$ (Calcium cyanamide)
50. (1) HCl , HNO_3 and H_2SO_4 form azeotrope at 20%, 68% and 98% respectively by mass of acid.
Therefore, HCl contains $\approx 20/100 = 1/5$
 HNO_3 contains $\approx 68/100 \approx 2/3$
 H_2SO_4 contains $\approx 98/100 \approx 3/3$
Thus, ordinary strong solution of HCl , HNO_3 and H_2SO_4 contains roughly $1/5$, $2/3$ and $3/3$ fractions of pure acid and water respectively.
51. (3)
52. (1)
53. (4)
54. (1)
55. (2)
56. (2)
57. (1) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
58. (3) $\text{Pb}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{PbO} + 2\text{NO}_2 + \text{O}_2$
59. (2) $2\text{NH}_3 + \text{CO}_2 \longrightarrow \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}$
60. (3) $\text{Mg} + 2\text{HNO}_3 \longrightarrow \text{Mg}(\text{NO}_3)_2 + \text{H}_2$
61. (4) $\text{NH}_2^\ominus + \text{N}_2\text{O} \longrightarrow \text{N}_3^\ominus + \text{H}_2\text{O}$
 $\text{NaNH}_2 + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{NH}_3$
62. (3) $\text{NCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{NH}_3 + 3\text{HOCl}(\text{X})$
63. (3) $\text{Cl}_2 + 4\text{NH}_3(\text{Excess}) \longrightarrow \text{N}_2 + 2\text{NH}_4\text{Cl}$
64. (4) Number of bond pairs = 4
Number of lone pairs = 0
65. (2) $\text{NO} + \text{NO}_2 \xrightarrow{-30^\circ\text{C}} \text{N}_2\text{O}_3$ (Pale blue)
66. (3) $\text{NO}_2^\oplus$ $\text{NO}_3^\oplus$ $\text{NH}_4^\oplus$
(sp) (sp^2) (sp^3)
50% p 67% p 75% p
Correct (3)
 $\text{NH}_4^\oplus > \text{NO}_3^\oplus > \text{NO}_2^\oplus$
67. (3) $\text{H}-\overset{\overset{\text{O}:\text{O}}{\parallel}}{\underset{\underset{\text{O}:\text{O}}{\parallel}}{\text{P}}}-\text{H}$ $\left[\begin{array}{l} 6 \text{ lp of } e^{-1's} \\ 6 \sigma \text{ bond} \\ 1 \pi \text{ bond} \end{array} \right]$
 $x = 6, y = 6, z = 1,$
 $\therefore x + y + z = 6 + 6 + 1 = 13$
68. (3) Correct (3):
M exhibits two O.S. + 3 and + 5, but covalency cannot be 5;
Hence M cannot expand its valence shell.
Therefore M will be nitrogen with two atomicity.
69. (4) Refer to note on P. 2.32 section 2.12.
70. (3) Refer to the structure on page. 2.5.
71. (3) Refer to the structure on page. 2.5 & 2.6.
72. (3) Factual
73. (3) Refer to structures on page 2.5.
74. (3) Since H_3PO_4 is tribasic and forms three series of salts.
75. (2) $\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow \text{POCl}_3 + 2\text{HCl} \xrightarrow{3\text{H}_2\text{O}} \text{H}_3\text{PO}_4 + 3\text{HCl}$
(A) (B) (C)



77. (1) (a) NF_3 (S_N1), NCl_3 (S_N2)
(b) P_4O_{10} (S_N1), SiCl_4 (S_N2)
(c) SF_4 , TeF_6 (Both S_N2)
(d) SiCl_4 , SiF_4 (Both S_N2)

78. (4) PH_3 is Lewis base and B_2H_6 is Lewis acid, So they react with each other.



81. (3) (i) NH_3
(ii) PH_3
(iii) PH_3 , NaH_2PO_2

82. (3) Refer to structures on Page. 2.5-2.6.

83. (1) When oxidation state of central atom is same, with the decrease in electronegativity of central atom, acidic character decreases.
Hence H_3PO_4 is most acidic.
 $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{H}_3\text{SbO}_4 > \text{H}_3\text{BiO}_4$

84. (1)

85. (4)

86. (1)

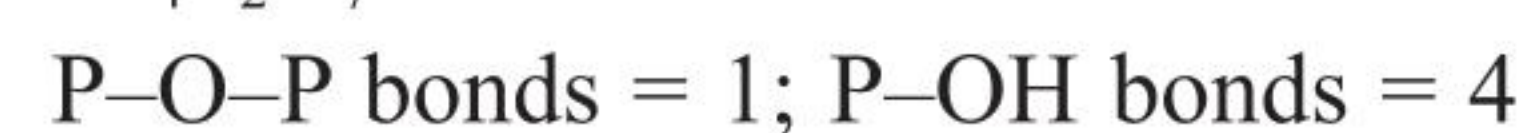
87. (2) Phosphide ion, P^{3-} . Hence, similar structure with $\text{Cl}^\ominus$

88. (2)

89. (1)

90. (1)

91. (3) $\text{H}_4\text{P}_2\text{O}_7$ Number of bonds are:



92. (2) $\text{P}_4 + 3\text{AgNO}_3 \longrightarrow \text{Ag}_3\text{P} + \text{NO}_2$

93. (4) $2\text{H}_3\text{PO}_4 \xrightarrow{240^\circ\text{C}} \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$

94. (4) $\text{P}_4 + \text{NaOH} \longrightarrow \text{PH}_3 + \text{NaH}_2\text{PO}_2 + \text{H}_2\text{O}$

95. (3)

96. (1)

97. (1)

98. (1)

99. (1)

100. (4) Due to high N-F bond strength, NF_3 is highly stable and hence inert towards hydrolysis.

101. (1)

102. (1)

103. (2)

104. (4)

105. (1)

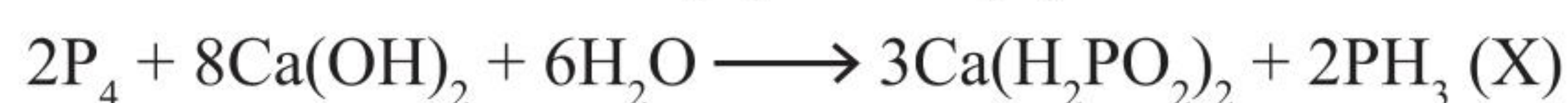
106. (1)

107. (2) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
 $\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$
 $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$

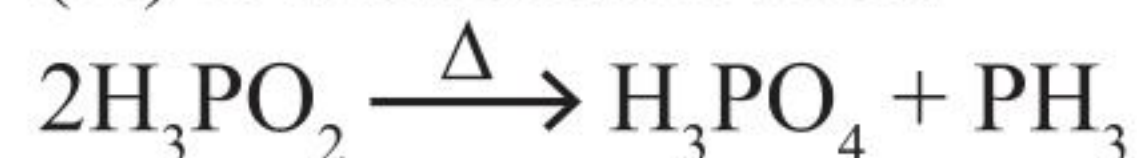
108. (2)

109. (2) White phosphorous + Lime water $\longrightarrow$

Calcium salt of an acid (A) + Gas (X)

(A) is H_3PO_2 , hypophosphorous acid.

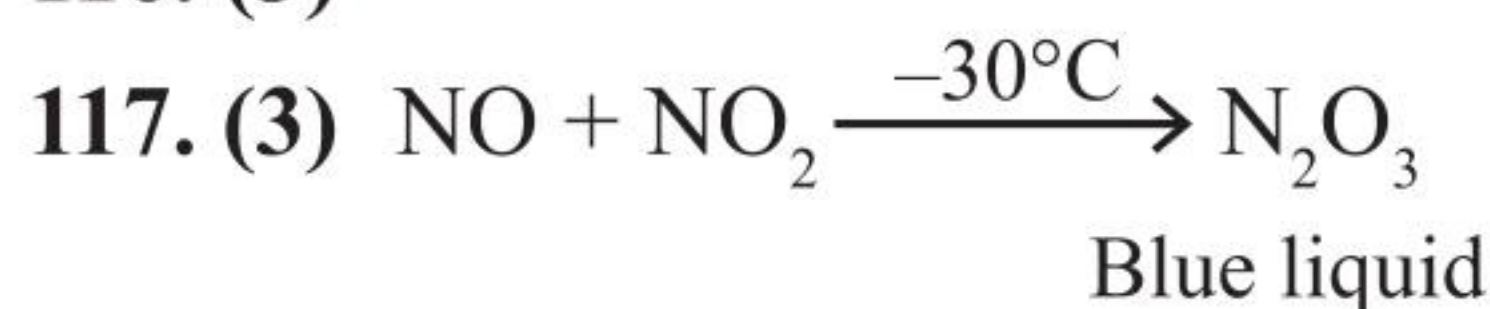
(A) is monobasic acid.

110. (1) $H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O$

1 mole Excess 1 mole

111. (2) The anhydride of HNO_2 is N_2O_3 . If O_2 is removed from N_2O_3 , then the resulting compound is N_2O . Nitrous acid supports combustion.112. (4) N_2O is laughing gas but linear in shape. NO_2 has pungent odour and angular in shape. NO is colourless gas and neutral.113. (1) PCl_5 exists as PCl_5 in gaseous state i.e. a covalent molecule. In solid state, it exists as $[PCl_4]^+ [PCl_6]^-$ an ionic compound.114. (4) $2NaOH + H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$ Only one hydrogen atom of H_3PO_4 is replaced, hence equivalent mass of H_3PO_4 is equal to its molecular mass.115. (1) O.S. of P is hypophosphorous acid, $H_3PO_2 = +1$

116. (3)

**Multiple Correct Answers Type**

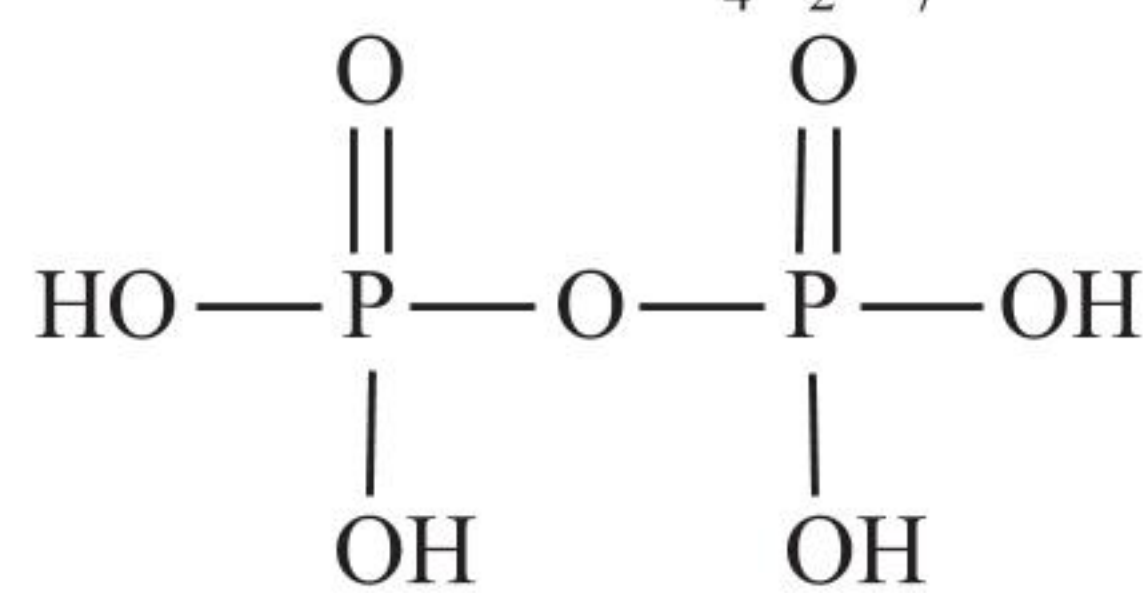
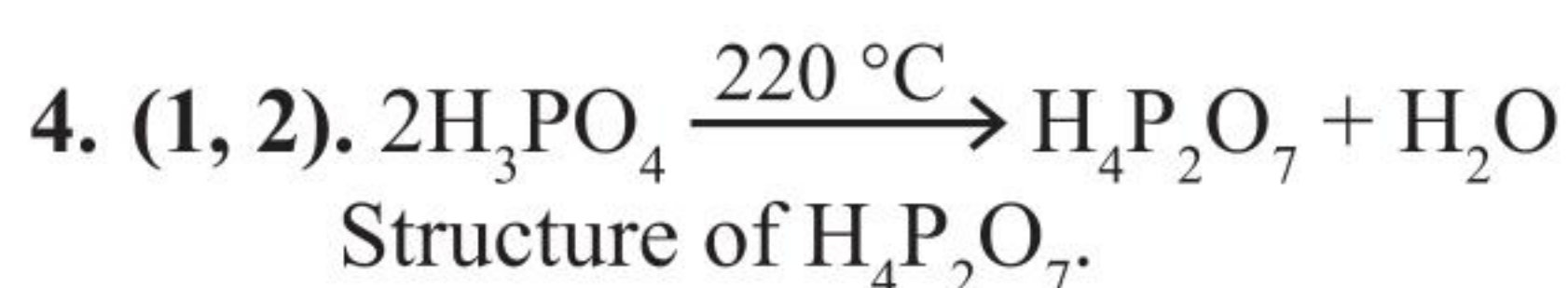
1. (1, 2, 4).

Only H_2S acts as reducing agent while HNO_2 , H_2O_2 and SO_2 act both oxidising and reducing agents.

2. (1, 2, 4).

While P_4 dissolves in CS_2 and also in $NaOH$ to form PH_3 and $H_2PO_2^-$ ion.Whereas red P_4 is not soluble in CS_2 and does not react with alkali solution.

3. (1, 2, 4). Factual



5. (1, 4)

 N_2 reacts with Mg and Al.

6. (2, 4)

It gives PH_3 and $H_2PO_2^-$.

7. (3, 4)

It is obtained by reaction (1) and (2).

8. (1, 2)

Statements (3, 4) are correct.

9. (1, 2, 3)

10. (3, 4)

11. (2, 3, 4)

Only statement (1) is true.

12. (1, 2, 3, 4)

13. (1, 2, 3)

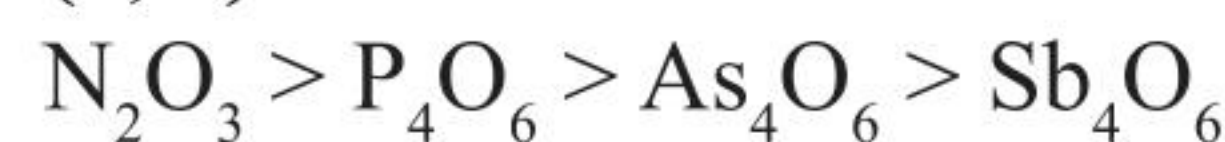
Correct (4)

 $N < P < Bi < Sb < As$

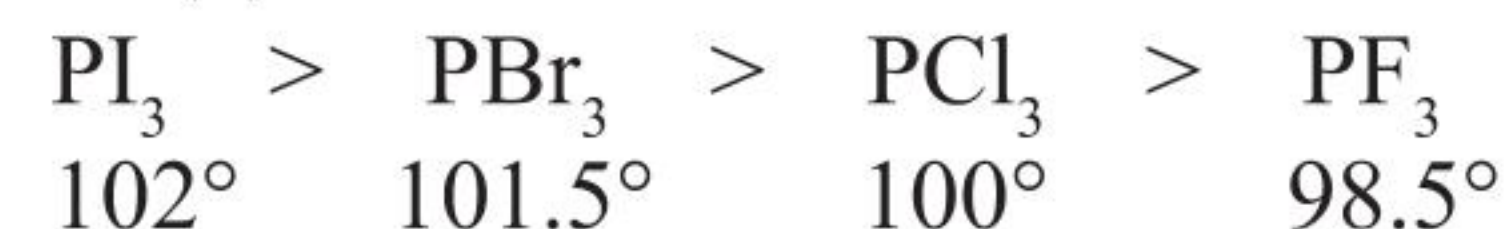
14. (1, 3, 4)

Correct (2) P_4O_6 , P_4O_8 and P_4O_{10} , all of them have 6(P—O—P) bonds

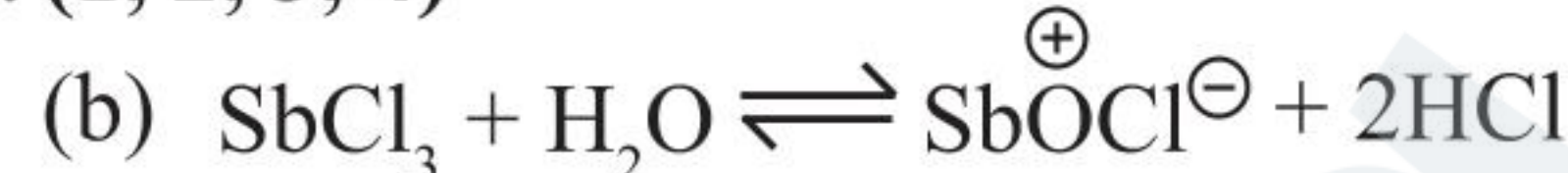
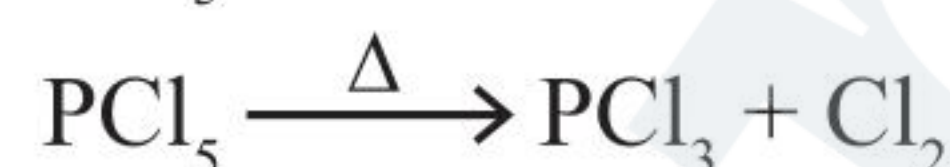
15. (1, 3)

 As_4O_6 and Sb_4O_6 are amphoteric while Bi_2O_3 is basic in nature.

Correct (4)



16. (1, 2, 3, 4)

Addition of excess of HCl suppresses the hydrolysis of $SbCl_3$ and shifts the equilibrium to the left.(c) NF_3 does not undergo hydrolysis due to high N—F bond strength.(d) PCl_5 is less stable due to its decomposition.

17. (1, 2, 4)

Correct (1), Not equal correct (2) In PCl_5 , axial bond is longer than equatorial bond.

18. (2, 3)



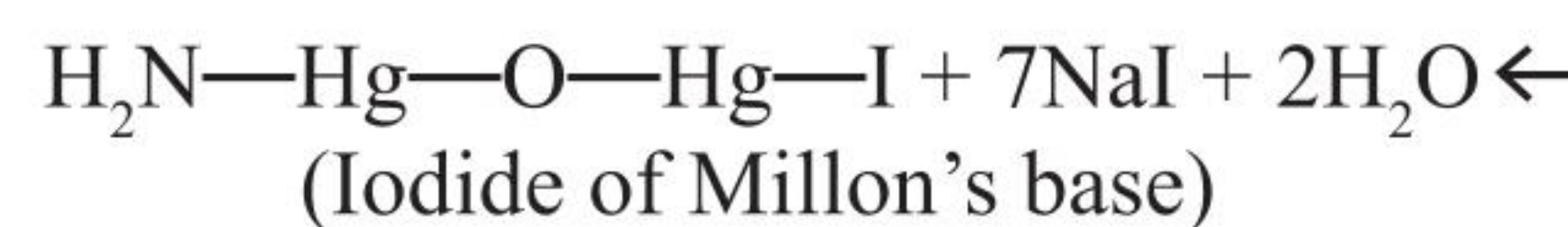
19. (1, 2, 3).

20. (1, 2).

21. (1, 2, 3). Refer to section 2.9.6

22. (1, 2, 3). Factual

23. (1, 3).



24. (2, 3)

25. (3, 4).

26. (3, 4).

27. (2, 3, 4).

Correct (1)

 NH_4NO_2 (ammonium nitrite) on heating gives $N_2O(g)$ 

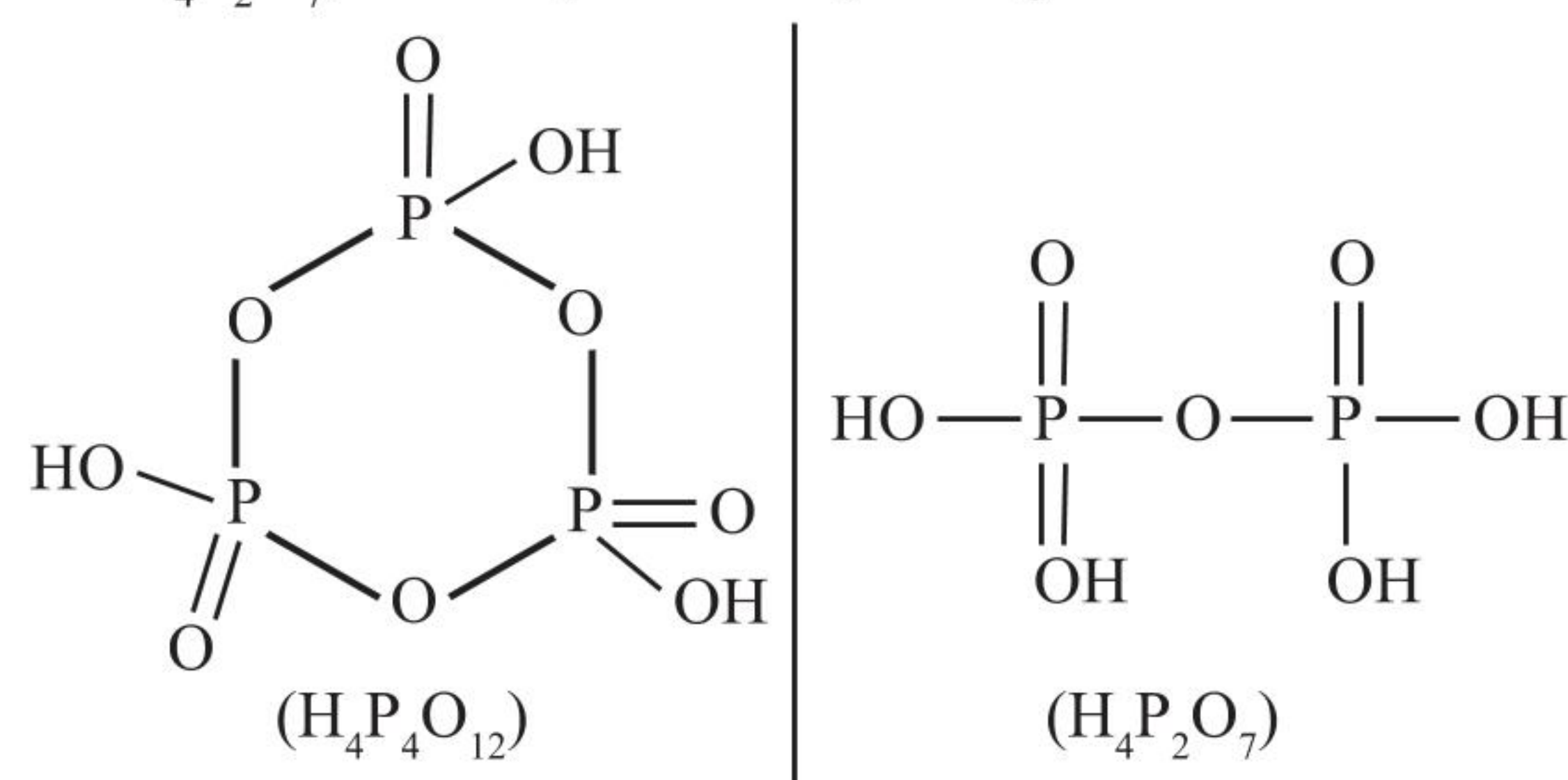
29. (1, 2)

30. (2, 3)

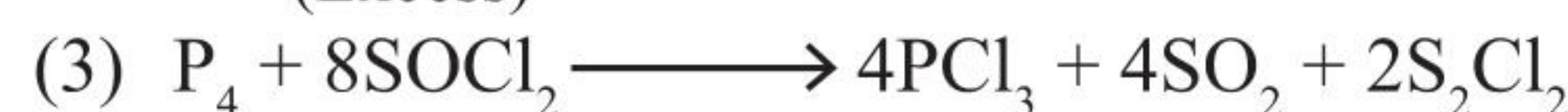
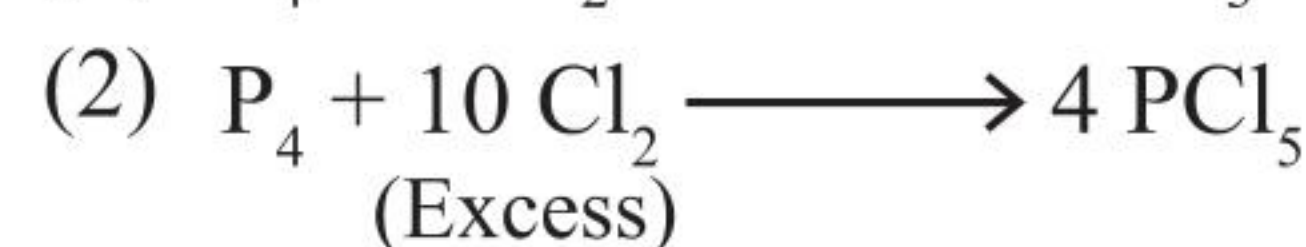
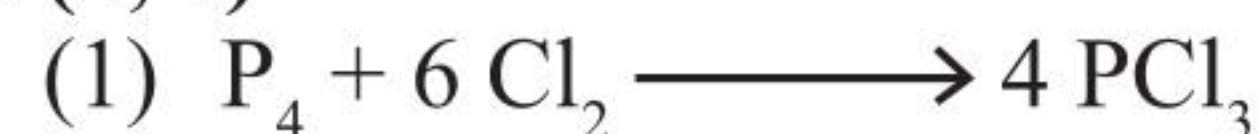
31. (2, 3). Refer to structures of $H_4P_4O_{12}$ and $H_4P_2O_7$.(a) $H_4P_4O_{12}$ is cyclic. $H_4P_2O_7$ is open chain.

(b) In both P is attached to 4-O-atoms.

(c) Both have same (P—O—P) linkage.

(d) In $H_4P_4O_{12}$, 4(P—O—P) linkageIn $H_4P_2O_7$, 2(P—O—P) linkage

32. (2, 4)



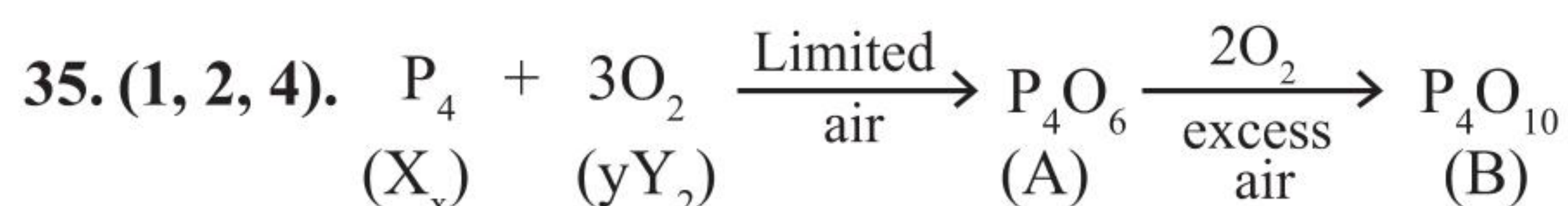
33. (1, 3). Refer to structure of P_4 .

Correct (1) It has 4 lp of e^- 's

Correct (3) It has 6 (p—p) single bond.

34. (4)

Correct (4) H_3PO_3 is weaker reducing agent than H_3PO_2 because it contains only one P—H bond while H_3PO_2 have two (P—H) bonds.



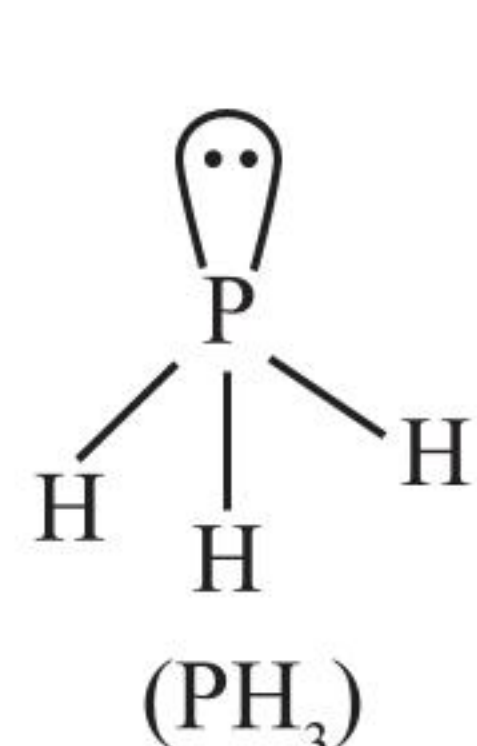
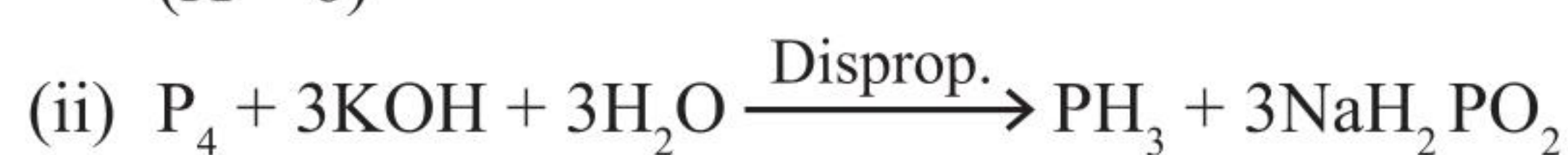
Bond length in $P_4O_6 >$ Bond length in P_4O_{10} .

Therefore,

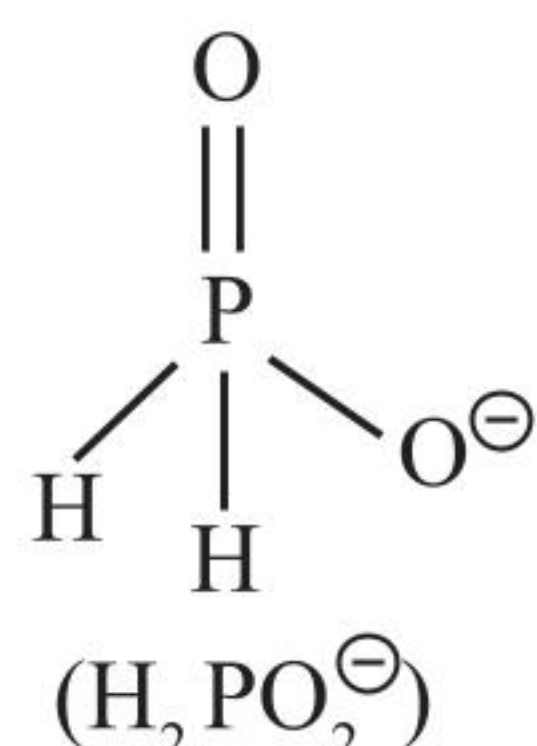
Bond angle (P—O—P) in $P_4O_6 <$ Bond angle (P—O—P) in P_4O_{10} .

$$\therefore x + y + z = 4 + 3 + 2 = 9$$

36. (1, 3, 4).



3(P—H) bond
Y = 3



2(P—H) bond
Y = 2

$$\therefore Y = 3 + 2 = 5$$

$$X - Y = 6 - 5 = 1$$

(1) is correct

Correct (2) is $\therefore$

$H_2PO_2^\ominus$ is formed in reaction (ii)

(3), (4) are correct.

37. (1, 2)

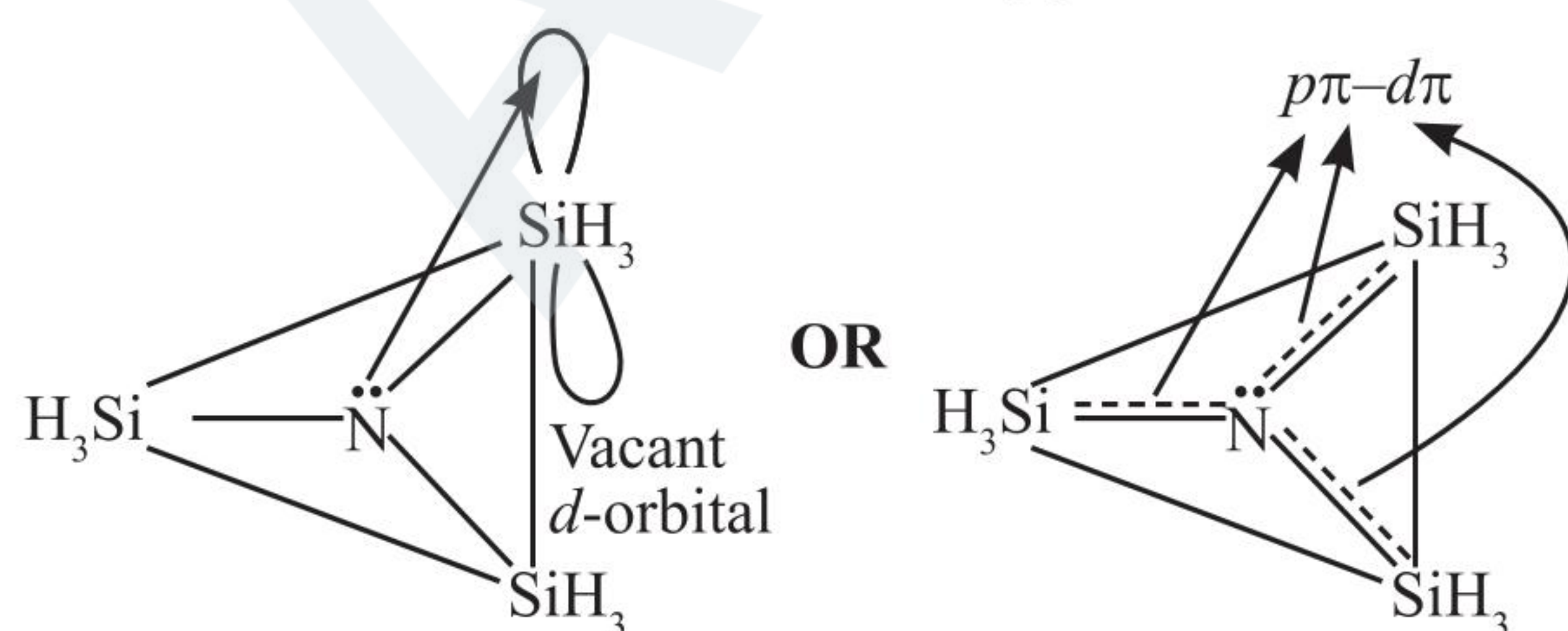
38. (1, 2, 3)

Linked Comprehension Type

Paragraph 1

1. (2) (I) $(SiH_3)_3\ddot{N}$ > (II) $(CH_3)_3\ddot{N}$ > (III) $\ddot{N}H_3$
Planar triangular Pyramidal Pyramidal
Bond angle $\approx 120^\circ$ Both $N(CH_3)_3$ and NH_3 are pyramidal, but CH_3 group is bulkier as compared to H, hence bond angle in $N(CH_3)_3$ is greater than NH_3 .

2. (3) Due to ($p\pi-d\pi$) multiple bonding in $(SiH_3)_3N$, shape is planar.



3. (3)

Paragraph 2

4. (3)

5. (2)

6. (4)

Paragraph 3

7. (1) $POCl_3$ is sp^3 hybridised with tetrahedral structure.

8. (3) $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

9. (2)

10. (3) Solid PCl_5 is $[PCl_4]^\oplus [PCl_6]^\ominus$.

$[PCl_4]^\oplus$ = Tetrahedral, $[PCl_6]^\ominus$ = Octahedral

Paragraph 4

11. (4)

12. (1) With the decrease in EN: ($F > Cl > Br > I$), tendency to donate lp of electron decreases, hence NF_3 is least basic.

13. (1) N due to absence of d-orbital in its valence shell cannot have a coordination number 5.

14. (2) Type of oxide remaining the same, M_2O_3 with the increase in electronegativity, acidic character increases, hence P_2O_3 is most acidic.

(EN of $P > As > Sb > Bi$)

15. (3) Due to weakest Bi—H bond strength, BiH_3 is least stable.

16. (2) Valence shell electronic configuration is ns^2np^3 . Hence number of unpaired electrons is 3.

17. (3) Since Bi is metallic, its halides are ionic.

Paragraph 5

18. (1) H_3PO_2 contains one P—OH group.

19. (2) Let oxidation state of P in H_3PO_3 is x
 $x(+1) \times 3 + x + (-2) \times 3 = 0$, $x = +3$

20. (3) Since H_3PO_3 is dibasic, it forms two series of salts.

21. (3) $H_3P_3O_9$ is $(HPO_3)_3$.

22. (4) Number of P=O bonds = 1

Number of P—OH bonds = 3

Matrix Match Type

Refer to Answer Keys.

Numerical Value Type

1. (5) N_2O , NO , N_2O_3 , NO_2 (or N_2O_4) and N_2O_5

2. (2) N_2 molecule exists as $:\text{N} \equiv \text{N}:$
Hence there are 2 lp's.

3. (3) Valence shell electronic configuration of group 15 elements is np^2np^3 . Hence, there are 3 unpaired electrons in the valence shell.

4. (6) There are 6 P—O—P bonds in P_4O_8 .

5. (4) In solid state, PCl_5 exists as $[PCl_4]^\oplus [PCl_6]^\ominus$
Hence there are 4P—Cl bonds in the cation.

6. (4) Pyrophosphoric acid, $H_4P_2O_7$ has 4P—OH groups.

7. (4)

8. (6) $8NH_3(\text{Excess}) + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$

9. (4) Phosphorous exists as P_4 . Hence atomicity = 4.

10. (6) (6 σ (N—O bonds)).

11. (4)

12. (1)

13. (5) $P = 3s^33p^33d^0$. Hence 5 vacant d-orbitals.

14. (4)

15. (2) $Ca_3P_2 + 3H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

16. (4) In white phosphorous, each P is sp^3 hybridised and forms 3P—P bonds. it has 1 lp. Hence in P_4 units, 4 lone pair of electrons are there.

17. (6) Bridging O-atoms in $P_4O_{10} = 6$.

18. (2) $P_4O_8 + 4H_2O \longrightarrow 2H_2PO_3 + 2H_3PO_4$

19. (2) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

20. (8)

21. (3.2)

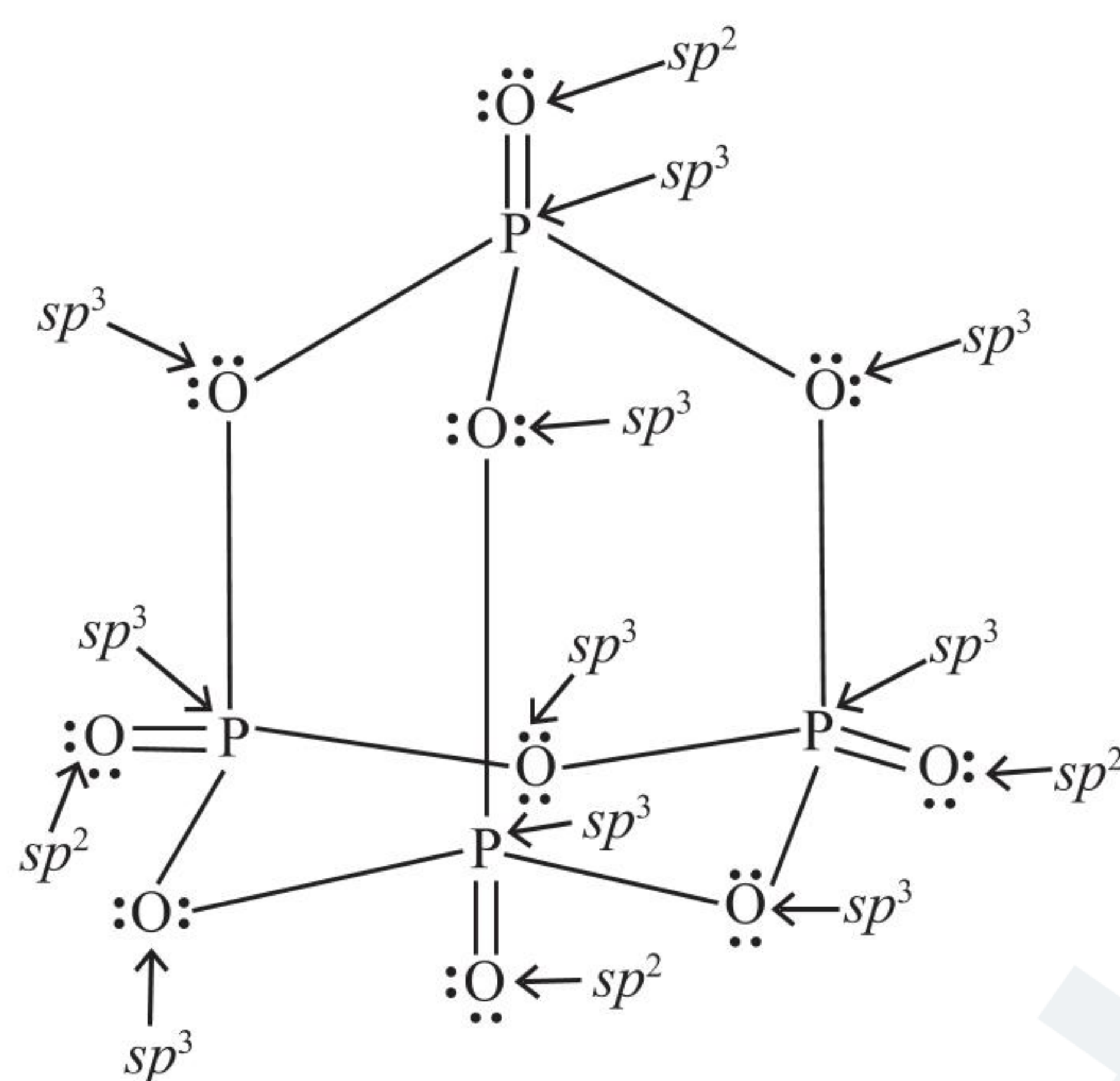
- | | | | |
|-------|----------|---------|--------------|
| (i) | N_2O | Neutral | Diamagnetic |
| (ii) | NO | Neutral | Paramagnetic |
| (iii) | N_2O_3 | Acidic | Diamagnetic |
| (iv) | NO_2 | Acidic | Paramagnetic |
| (v) | N_2O_4 | Acidic | Paramagnetic |
| (vi) | N_2O_5 | Acidic | Diamagnetic |

$$X = 2, Y = 2$$

$$\therefore (X + Y)^2 = \frac{(4)^2}{5} = 3.2$$

22. (2.5)

Structure of P_4O_{10} :



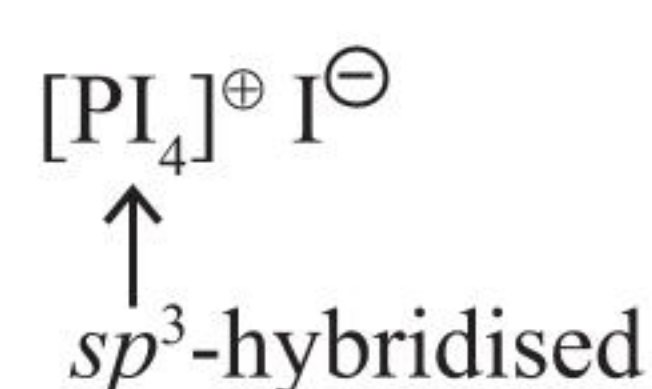
All four 'P' atoms are sp^3 hybridised six 'O' atoms are sp^3 hybridised.

Four 'O' atoms are sp^2 hybridised.

Total sp^3 hybridised atoms in $P_4O_{10} = 4 + 6 = 10$

Total sp^2 hybridised atoms in $P_4O_{10} = 4$.

(ii) Solid PI_5 exists as



Total number of sp^3 hybridised atoms in

$PI_5 =$ one.

Total number of sp^2 hybridised atoms in $PI_5 =$ zero

$$\therefore X = 10 + 1 = 11$$

$$Y = 4 + 0 = 4$$

$$\frac{(X + Y)}{6} = \frac{15}{6} = 2.5$$

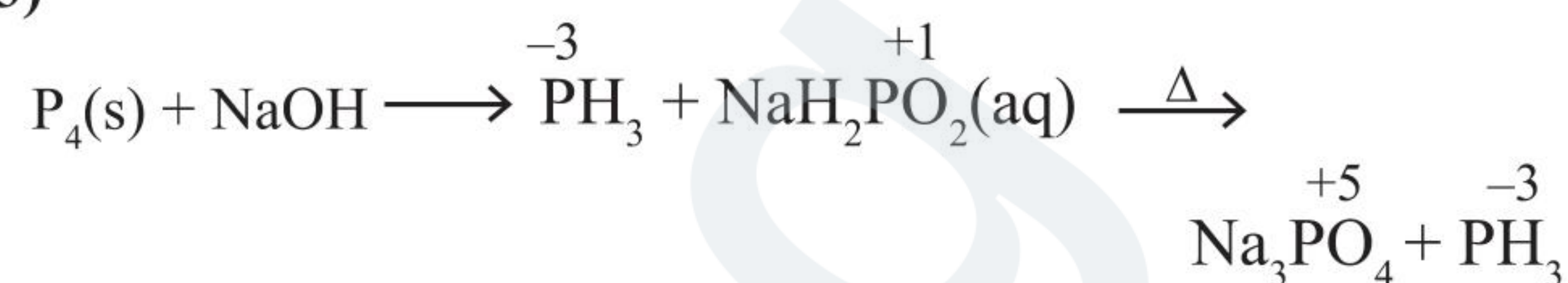
2. $NH_4NO_3 \xrightarrow{\Delta} N_2O(g) + H_2O(g)$

3. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2(g) + H_2O(g) + Cr_2O_3(s)$

4. $Ba(N_3)_2 \xrightarrow{\Delta} Ba(s) + 2N_2(g)$ (Pure)

Note: In reaction (d), we will get pure N_2 as no other gas is evolved.

3. (3)



Oxidation state of P in PH_3 and Na_3PO_4 are -3 and $+5$ respectively. It is a disproportionation reaction.

4. (2) $HNO_3 = +5$, $NO = +2$
 $NH_4Cl = -3$, $N_2 = 0$

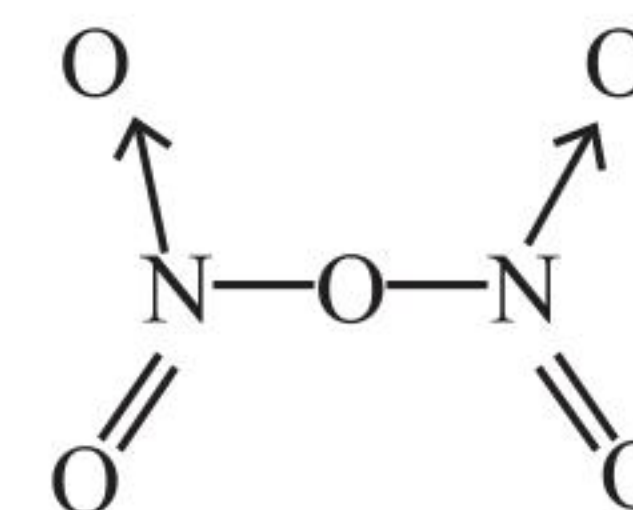
5. (1) $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

Species	Oxidation state of P
H_3PO_4	+5
$H_4P_2O_6$	+4
H_3PO_3	+3
H_3PO_2	+1

Multiple Correct Answers Type

1. (1, 2, 3)

N_2O_5 does not have an N—N bond, others have



2. (2, 4)

It produces N_2O_5



(a) **True:** $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(b) **True:** $O = N - O - N = O$ is diamagnetic



(c) **False:** N_2O_5 doesn't contain N—N bond, it contains (N—O—N) bond

(d) **True:** $N_2O_5 + Na \longrightarrow NaNO_3 + NO_2 \uparrow$ (Brown gas)

3. (2, 3)

(a) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ (N_2O can further decompose to N_2 and O_2 at temperature above $300^\circ C$)

(b) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

(c) $Ba(N_3)_2 \xrightarrow{\Delta} 3N_2 + Ba$

(d) Mg_3N_2 does not decompose at any temperature.

4. (1, 2, 3)

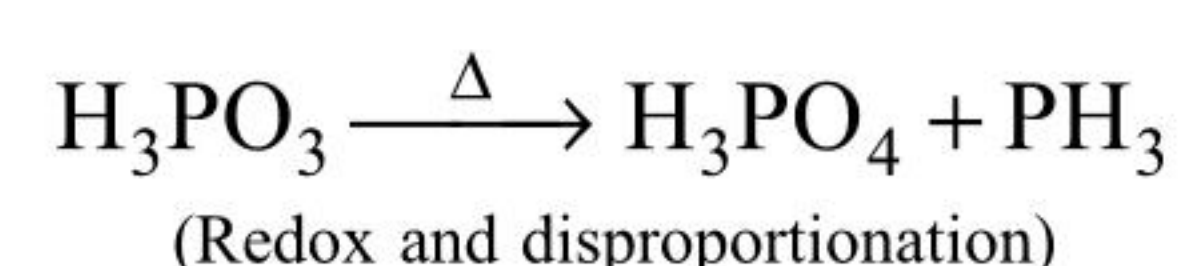
Bi_2O_5 is more basic than N_2O_5 .

NF_3 is more covalent than BiF_3 .

PH_3 boils at lower temperature than NH_3 .

N—N single bond is weaker than P—P single bond.

5. (1, 2, 4)



Archives

JEE Advanced

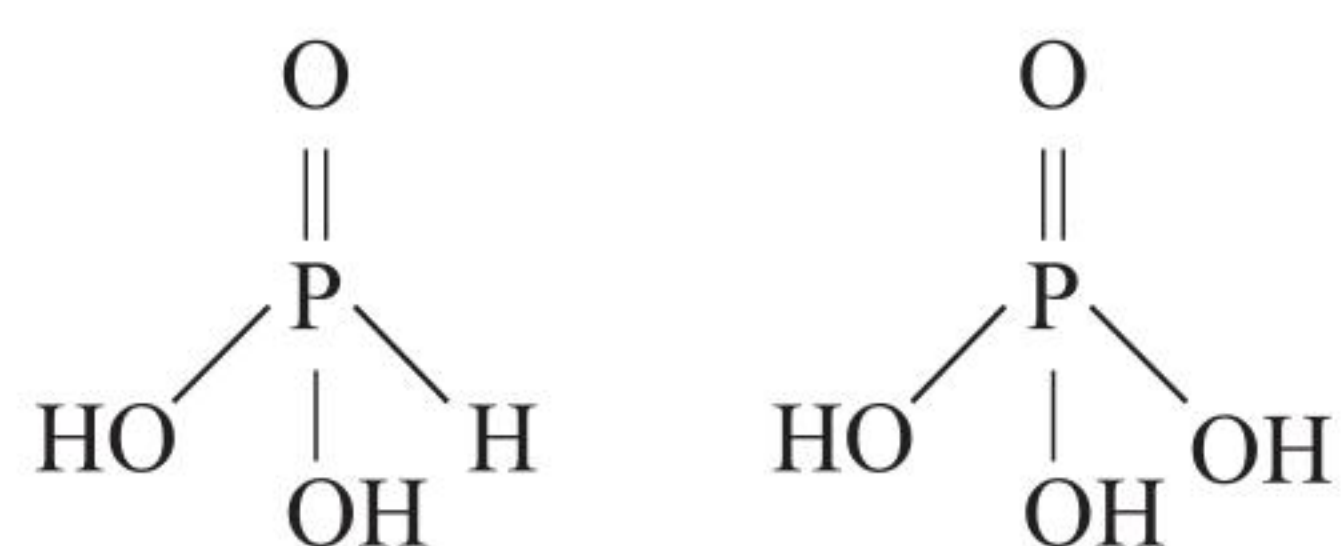
Single Correct Answer Type

1. (2) $P_4 + 3O_2 \xrightarrow{N_2} P_4O_6$

N_2 retards further oxidation of P_4O_6 .

2. (4)

1. $NH_3 + CuO \xrightarrow{\Delta} N_2(g) + Cu(s) + H_2O$

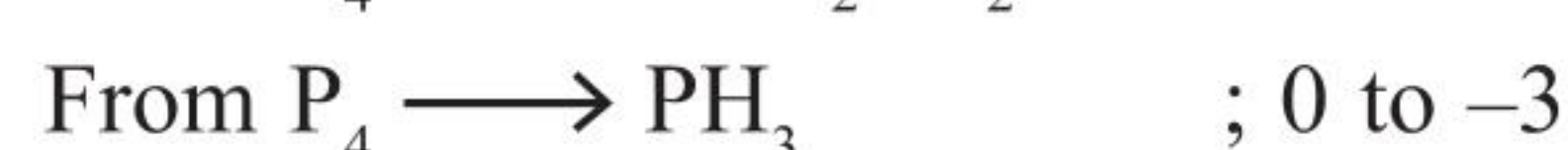
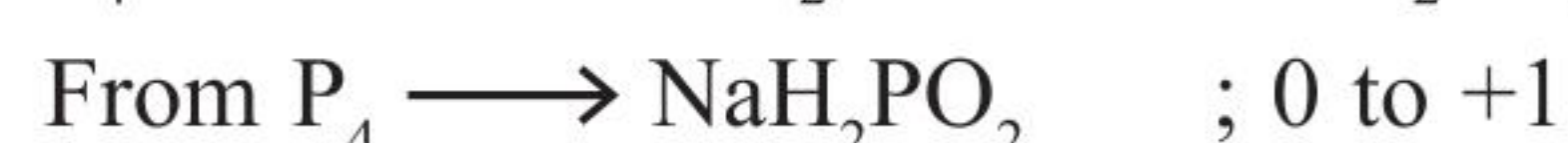


It is a dibasic acid and due to presence of P—H bond, it is reducing agent but same is not possible for H_3PO_4 as it has 3 O—H groups.

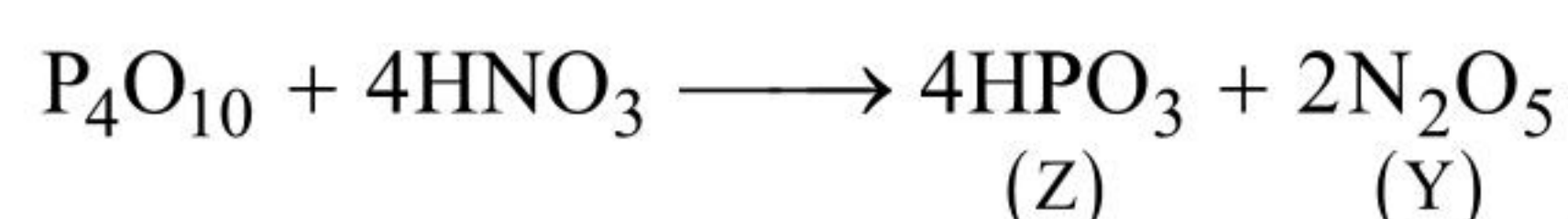
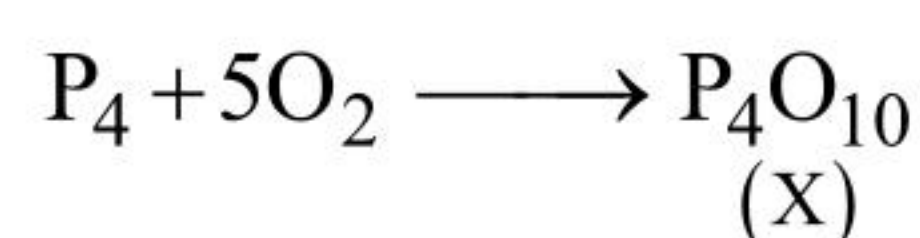
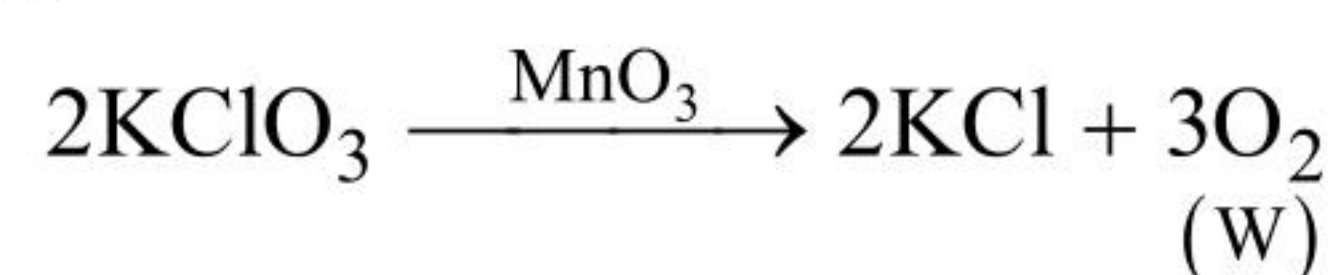
Linked Comprehension Type

- (3) Between nitrates and phosphates, nitrates are less abundant in the earth's crust because most of them are soluble in water.
- (3) Both NH_3 and PH_3 are sp^3 hybridised with pyramidal in shape. NH_3 is a better electron donor than phosphine because the lone pair of electrons occupies the sp^3 -orbital and is more directional. It is easily donatable. Due to small size of N, the lone pair electron density is higher in NH_3 , than in PH_3 , so NH_3 is better electron donor.

- (2) Oxidation state increases as well as decreases, so this is called disproportionation reaction.



- (2) – 5. (3)



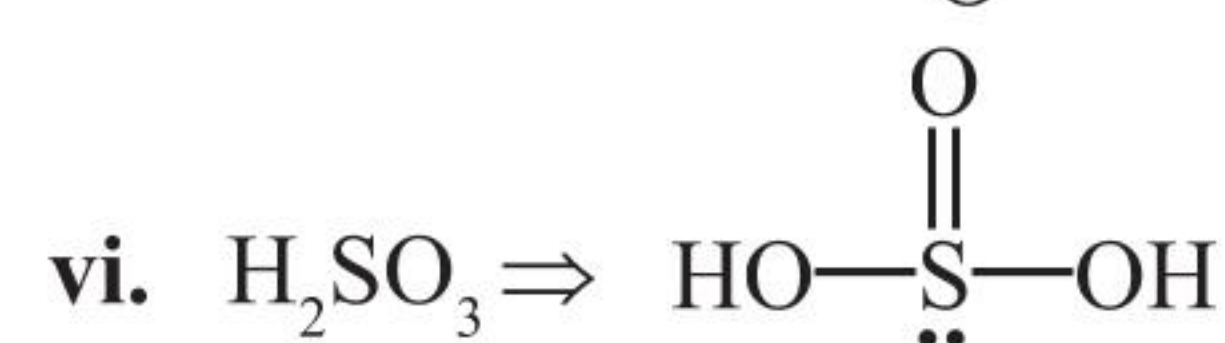
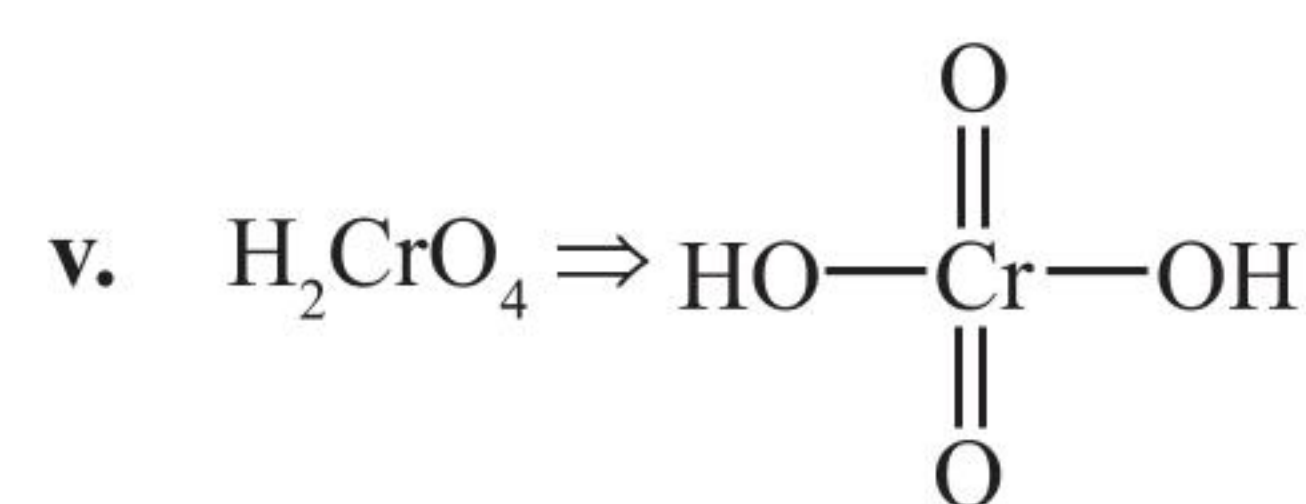
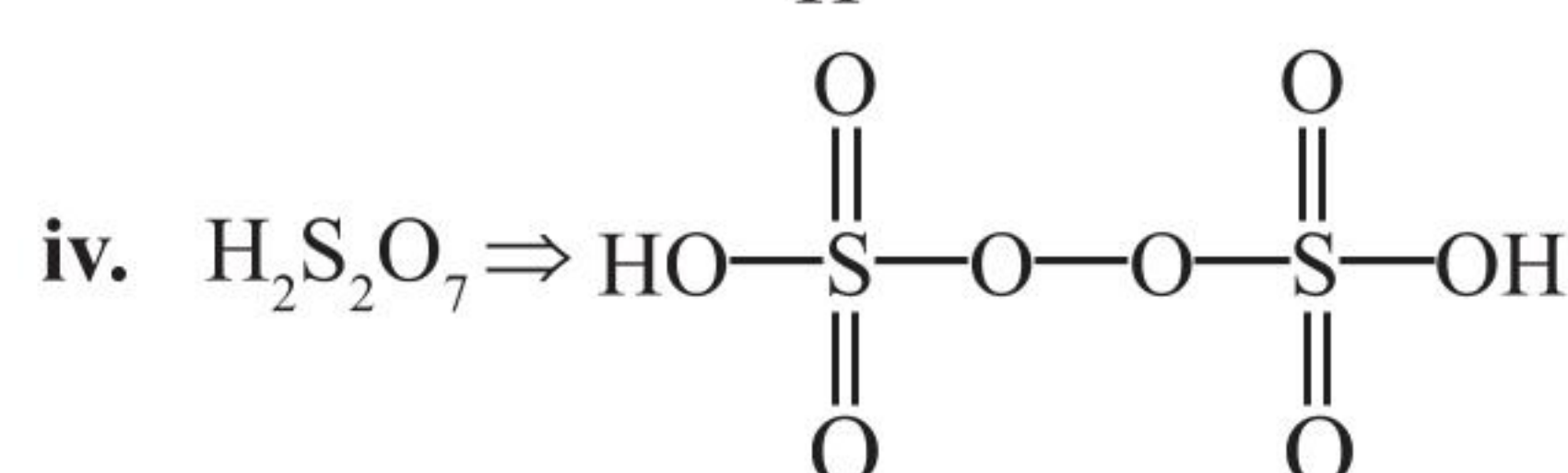
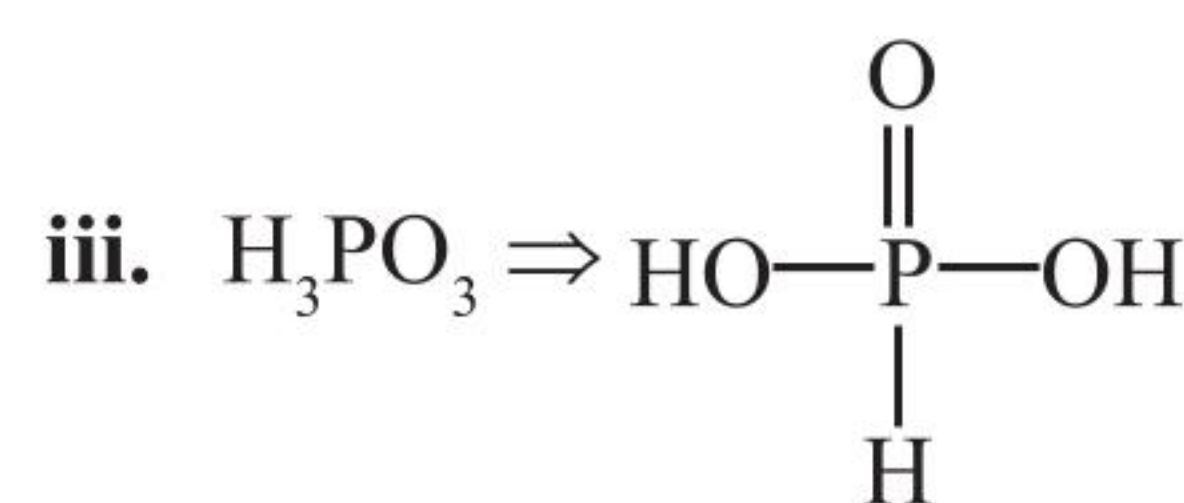
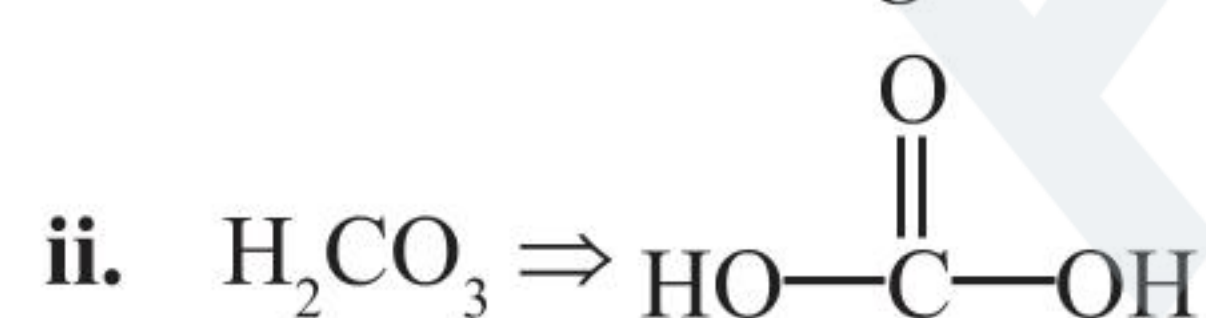
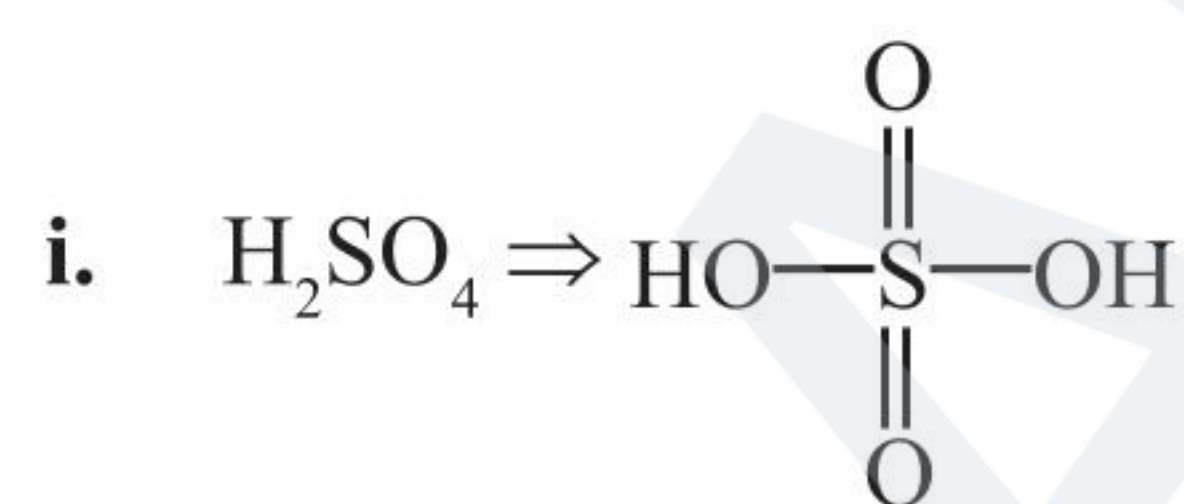
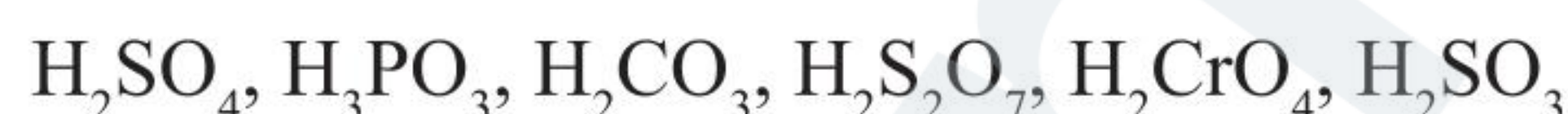
Matrix Match Type

- (a) p, s (b) q, s (c) r, t (d) q, t
 - $3\text{Cu} + (\text{dil.}) 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
 - $3\text{Cu} + (\text{conc.}) 4\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
 - $4\text{Zn} + (\text{dil.}) 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
 - $\text{Zn} + (\text{conc.}) 4\text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{NO}_2 + 2\text{H}_2\text{O}$

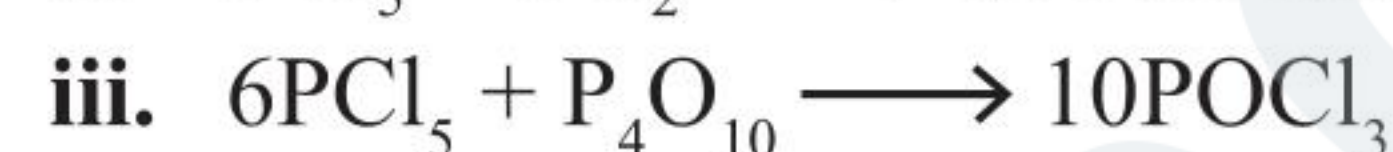
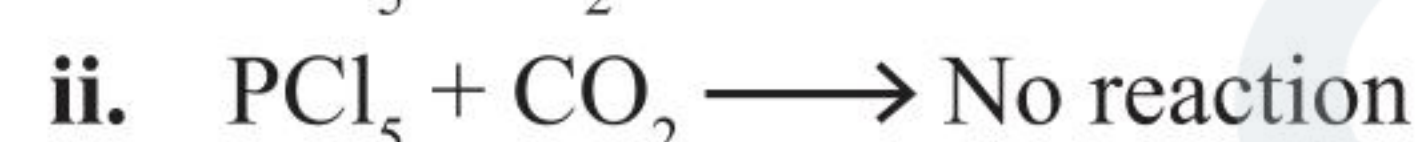
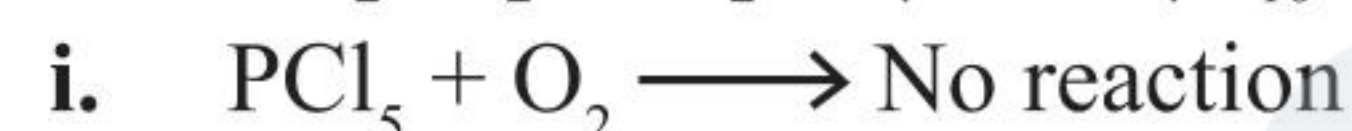
Numerical Value Type

- (6)

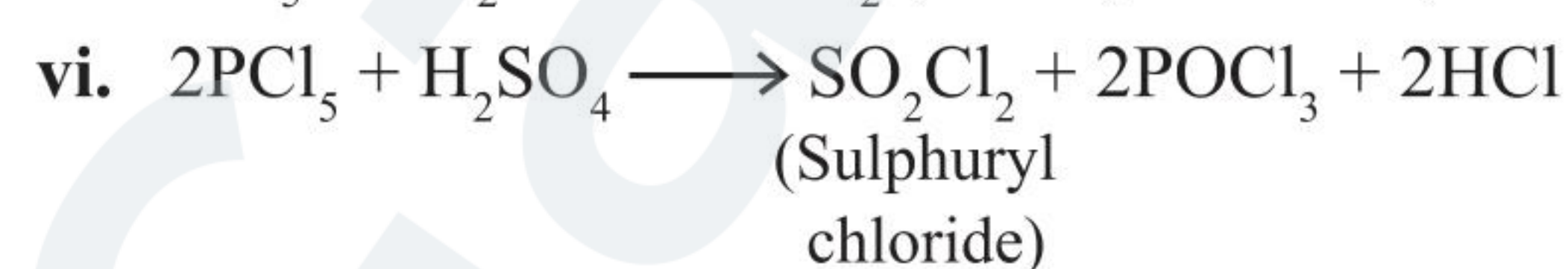
The total number of diprotic acids among the following are:



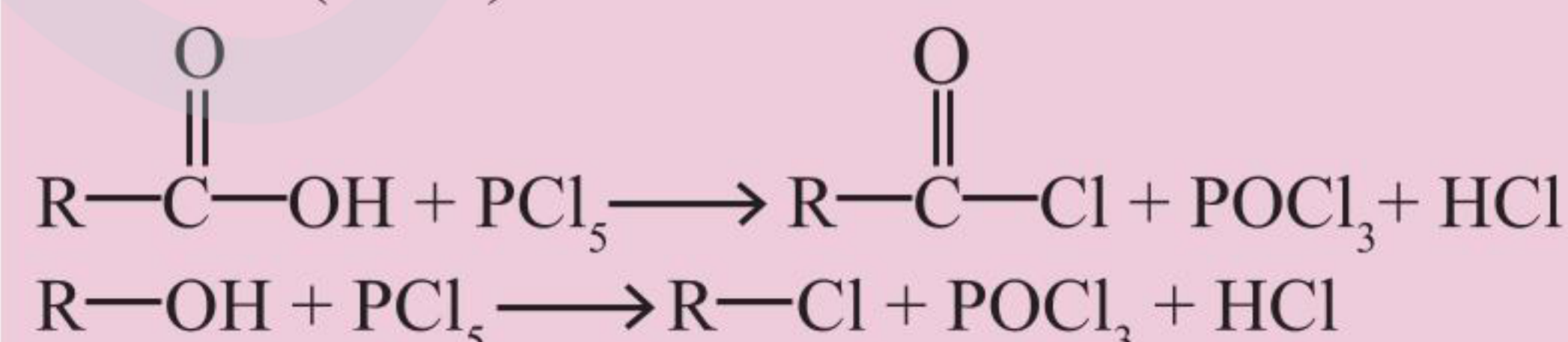
- (4) $\text{SO}_2, \text{H}_2\text{O}, \text{H}_2\text{SO}_4$ and P_4O_{10}



- With limited amount of H_2O ; PCl_5 gives POCl_3 but with excess of water it does not give POCl_3 but gives H_3PO_4 .



Note: PCl_5 also reacts with carboxylic acids (RCOOH) and with alcohols (ROH) as :



- (6)

